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PACKAGING

V. THE GREASE RESISTANCE OF SOME COMMON PACKAGING MATERIALS[1]

BY C. G. LAVERS[2]

Abstract

The grease resistance of a wide variety of packaging materials was tested before and after creasing and ageing, using a modification of TAPPI method T454 *m*-44. Kraft and sulphite were of little or no value as grease barriers even after paraffin wax coating or impregnating. Vegetable parchment and 'greaseproof' paper were superior to kraft. The grease resistance of glassine was 5 to 10 times greater than that of either greaseproof paper or vegetable parchment. Polyethylene, in turn, was considerably more resistant than glassine, and just slightly less resistant than all grades of "Cellophane", and cellulose acetate, cellulose nitrate, ethyl cellulose, Pliofilm, vinylite, and Saran.

Creasing glassine caused large reductions in its grease resistance, especially when heavy basis weights were tested. Paraffin wax coatings seemed to be more effective in improving grease resistance when dense base stocks were used. On kraft, a heavy wax coating was necessary to produce a small improvement, while on glassine only a very light coating was required, to bring about considerable improvement in grease resistance. Ageing many materials at 140° F. markedly reduced their grease resistance. An exception to this was glassine, most samples of which had greater resistance to grease penetration after ageing. Neither ageing nor creasing appreciably affected the grease resistance of Cellophane, or the thermoplastic films tested.

Introduction

To design a suitable package for a particular food, a knowledge of the mechanical strength, water-vapour resistance, sealing properties, grease resistance, etc., of many packaging materials is usually necessary. Earlier publications in this series have dealt with the water-vapour transmission and mechanical strength of several packaging materials (2, 3). The purpose of the present study is to evaluate the grease resistance of many of the materials commonly used in food packaging.

Materials and Methods

The materials tested included kraft, sulphite, cellucine, glassine, vegetable parchment, manilla, 'greaseproof' paper, "Cellophane", and several thermoplastic films including cellulose acetate, cellulose nitrate, ethyl cellulose, vinylite, polyethylene, Saran, and Pliofilm. Many of the materials were

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examined in both the waxed and unwaxed states and at several different basis weights. A detailed description of all samples studied is given in Table I.

The method of testing grease resistance was essentially that described in TAPPI method T454 *m*-44, with certain modifications. By this method a small pile (5 gm.) of sand is placed on the sample to be tested, to this is added 1.1 ml. of turpentine containing a red dye, and the time required for the coloured turpentine to penetrate the sample and stain a sheet of white paper placed beneath it is measured. The samples were not conditioned and tested at a fixed temperature and humidity as required by T454 *m*-44, all determinations being done at room conditions (approximately 75° F., 35% relative humidity). The TAPPI standard test for grease resistance also states that 30 specimens of each sample should be tested. In this study 15 specimens of unaged, and five of aged, samples were tested. This reduction in the number of specimens tested was believed to be justified because preliminary trials had shown that variations between samples of one type of material from different sources were greater than the variations between different specimens of a single sample. Since samples were available from a single source only and were often taken from the same roll, it was considered that the number of determinations done gave sufficiently accurate values for a particular sample, and for setting up a relative scale for comparing the various materials.

The relative scale used was as follows:

Time for dye to penetrate sample, sec.	Grease resistance score
0 – 50	0
50 – 500	1
500 – 1000	2
1000 – 2000	3
2000 – 4000	4
4000 – 8000	5
8000 – 18000	6
>18000	7

The large number of determinations that had to be done necessitated the adoption of a more convenient procedure than moving each sample to see if penetration had occurred. To overcome this difficulty, a low platform (18 in. high) with a glass top was placed on the laboratory bench. This was illuminated from below with a fluorescent light of suitable length. Samples were then placed on the top of the glass sheet, replacing the white book paper of T454 *m*-44 with a thin tissue that the coloured turpentine penetrated instantly. With this arrangement test specimens could easily be examined for penetration from underneath without moving any samples, making it possible to do many determinations simultaneously.

Since the grease resistance of a creased sheet may be considerably less than that of the uncreased material, samples were tested both before and after

creasing. The method of creasing has been described.* Briefly it consists in making two creases in the material crossing at right-angles by folding first in one direction and then in the opposite, the crease being produced by placing a 1 lb. weight on the loosely folded material.

To simulate long term storage under dry conditions samples were aged for one week at 140° F., low humidity (approximately 6%), conditioned for 24 hr. at room temperature and humidity, and their grease resistance subsequently tested.

Results

Grease resistance scores are given in Table I. Values that are recorded as 7 indicate that penetration did not occur in five hours. Tests were not run longer than this because it was found that at the end of five hours almost all the turpentine had evaporated.

When untreated (i.e., unwaxed, not laminated, and not aged or creased) base stocks were considered, it was obvious that kraft and ordinary sulphite papers were of little or no value as grease barriers. Vegetable parchment and 'greaseproof' paper had approximately equal resistances, and were superior to kraft. Although the values obtained for greaseproof paper were rather low, materials of this type can be produced with very high grease resistance, as shown by the commercial sheets designated in Table I as Lard Liners and Shortening Papers. The very high resistance of these materials was probably a result of the type of pulp used, and the treatment applied to it in the beater (1). The grease resistance of most samples of glassine was 5 to 10 times greater than that of either greaseproof paper or vegetable parchment. Polyethylene was considerably more resistant than most samples of glassine, but less resistant than Cellophane, cellulose acetate, cellulose nitrate, ethyl cellulose, Pliofilm, vinylite, and Saran.

Creasing unwaxed and unaged samples of many materials caused considerable reduction in their grease resistance. This was especially noted with glassine. For this material, the reduction in grease resistance score upon creasing became greater as the basis weight of the sample increased. Creasing did not appreciably affect the grease resistance of Cellophane or the various thermoplastic materials tested.

The effectiveness of paraffin wax in improving grease resistance appeared to depend largely on the nature of the base sheet to which it was applied. On kraft, dry waxing, i.e., wax impregnating, had little beneficial effect. Kraft, paraffin coated on one side, did not show any improvement in grease resistance until a basis weight of 60 lb. per ream (ream weights refer to 500 sheets, 24 by 36 in.) was used with a 12 lb. wax coat. Samples coated on both sides showed some resistance when 25 lb. material was waxed to 35 lb.

* *Wrapping greaseproof. Canadian Packaging Committee Code 105. Sept. 15, 1945. Currently available from Forest Products Laboratories, Department of Mines and Resources, Ottawa, Canada.*

TABLE I

THE GREASE RESISTANCE OF SOME COMMON PACKAGING MATERIALS

Material		Grease resistance score			
		Materials as received (average 15 determinations)		Materials aged one week at 140° F. (average 5 determinations)	
		Flat	Creased	Flat	Creased
Kraft					
50 lb.		0	0	0	0
30 lb. dry waxed to 36 lb.		0	0	0	0
45 lb. dry waxed to 55 lb.		0	0	0	0
15 lb. waxed one side to 20 lb.	Wax up	0	0	0	0
	Wax down	0	0	0	0
28 lb. white, waxed one side to 31 lb.	Wax up	0	0	0	0
	Wax down	0	0	0	0
30 lb. waxed one side to 38 lb.	Wax up	0	0	0	0
	Wax down	0	0	0	0
60 lb. blue, waxed one side to 72 lb.	Wax up	1	0	1	0
	Wax down	3	0	1	0
25 lb. waxed two sides to 35 lb.		2	0	1	0
25 lb. waxed two sides to 50 lb.		2	0	1	0
45 lb. waxed two sides to 65 lb.		3	0	1	0
80 lb. waxed two sides to 105 lb.		4	0	3	0
25 lb. coated one side with a flexible wax composition to 65 lb.	Wax up	5	3	5	4
	Wax down	4	3	5	4
25 lb. wax laminated (5 lb. wax) to 25 lb., thermoplastic coated	Coating up	3	0	0	0
	Coating down	1	0	0	0
Sulphites					
20 lb. dry waxed to 24 lb.		0	0	0	0
30 lb. dry waxed to 38 lb.		0	0	0	0
40 lb. dry waxed to 48 lb.		1	0	0	0
20 lb. unfilled, waxed two sides to 30 lb.		1	0	0	0
20 lb. filled, waxed two sides to 30 lb.		1	0	1	0
Manilla					
48 lb. waxed two sides to 67 lb.		3	0	2	0
Cellucine					
20 lb. waxed two sides to 25 lb.		1	0	1	0
Vegetable parchments					
27 lb.		1	1	1	1
40 lb.		2	1	1	1
27 lb. waxed one side to 34 lb.	Wax up	2	1	2	1
	Wax down	3	1	2	1
27 lb. waxed two sides to 33 lb.		1	1	2	1
'Greaseproof' papers					
20 lb. full-bleached		1	1	1	1
25 lb. full-bleached		1	1	1	1
30 lb. full-bleached		1	1	1	1
35 lb. full-bleached		1	1		
40 lb. full-bleached		3	1	2	1
25 lb. semibleached		1	1	1	1
25 lb. full-bleached, wet strength		1	1	2	1

TABLE I—*Concluded*

THE GREASE RESISTANCE OF SOME COMMON PACKAGING MATERIALS—*Concluded*

Material	Grease resistance score			
	Materials as received (average 15 determinations)		Materials aged one week at 140° F. (average 5 determinations)	
	Flat	Creased	Flat	Creased
Lard liners				
30 lb. full-bleached, semiplastic	3	2	3	1
40 lb. full-bleached	7	7	7	5
Shortening papers				
25 lb. superplastic	4	3	7	7
35 lb. superplastic	5	4	7	7
44 lb. superplastic	7	7	7	7
Glassines				
20 lb. full-bleached	5	3	5	5
25 lb. full-bleached	4	2	3	2
30 lb. full-bleached	6	1	4	3
40 lb. full-bleached	6	1	3	1
25 lb. full-bleached, opaque	2	1	1	1
40 lb. full-bleached, opaque	3	1	1	1
25 lb. full-bleached, opaque, plasticized	2	1	2	1
30 lb. full-bleached, plasticized	5	2	5	4
25 lb. semibleached	3	1	4	3
25 lb. red	3	3	3	3
25 lb. red, plasticized	1	1	3	2
20 lb. amber	3	1	3	3
25 lb. amber	2	1	3	1
30 lb. amber	4	2	4	2
25 lb. yellow	2	2	4	1
28 lb. yellow	3	1	4	1
25 lb. chocolate	1	1	3	2
25 lb. blue	3	3	4	3
25 lb. waxed two sides to 28 lb.	7	7	7	7
55 lb. wax laminated, bleached	7	7	7	7
25 lb. wax laminated to 25 lb. kraft	7	7	7	7
Cellophanes				
300 P.T.	7	7	7	7
300 M.S.T.	7	7	7	7
300 M.S.A.T.	7	7	7	7
300 M.S.Y.T.	7	7	7	7
Thermoplastics				
Polyethylene (0.003 in.)	6	6	6	6
Saran (0.002 in.)	7	7	7	7
Vinylite (0.002 in.)	7	7	7	7
Pliofilm (0.002 in.)	7	7	7	7
Cellulose acetate (0.002 in.)	7	7	7	7
Cellulose nitrate (0.003 in.)	7	7	7	7
Ethyl cellulose (0.005 in.)	7	7	7	7

None of the paraffin waxed kraft samples showed any grease resistance after folding. The kraft sample coated 40 lb. per ream with a flexible wax compound had a much greater transudation time than paraffin coated samples, and retained considerable resistance after folding. The sample of 60 lb. kraft, paraffin coated on one side to 72 lb., showed considerably greater grease resistance when the unwaxed side of the sheet was next to the turpentine; however for the sample coated with a flexible wax compound the opposite was true. The explanation for this is not apparent. Wax laminating two sheets of kraft effected no improvement in grease resistance after folding. Samples of paraffin waxed sulphite were no better than similar samples of waxed kraft.

While only one sample of each of manilla and cellucine were tested, paraffin waxed manilla had a resistance similar to that of waxed kraft, and waxed cellucine was little better than waxed kraft. Paraffin coated vegetable parchment required less wax than kraft paper to effect an improvement in grease resistance but, as with kraft, wax-coated vegetable parchment was no better than the unwaxed material after creasing. The results obtained with samples of paraffin coated vegetable parchment indicated that for a given weight of wax-coating, greater grease resistance could be achieved by putting all the wax on one side of the paper, rather than by dividing it between the two sides. Vegetable parchment, paraffin coated on one side, had greater resistance when the unwaxed side was toward the turpentine. Since paraffin coated kraft behaved in a similar manner it appears that papers coated on one side with paraffin should be used with the unwaxed side toward the greasy surface.

Application of a very light paraffin wax coating to glassine markedly improved its grease resistance both before and after creasing, and wax laminating glassine to glassine, or glassine to kraft, raised the grease resistance score far above that of either sheet alone. The results indicate that the more dense the base stocks, the more effective wax coatings become in enhancing the grease resistance of paper.

Ageing many materials at 140° F. markedly reduced their grease resistance. The major exceptions to this were Shortening papers and glassine, many samples of which had greater resistance to grease penetration after ageing. The resistance of creased samples of these stocks was markedly improved by ageing. When they were aged, much of the wax ran off the kraft samples that were coated with paraffin, and the material assumed the appearance of a dry waxed sheet. Ageing the kraft sample coated with a flexible wax compound did not lower the grease resistance score of the uncreased material, and creased samples had a greater resistance after ageing. The probable reason for this is that the temperature was not high enough to cause the wax to run off the paper, although it was sufficiently high to cause some of it to soak into the sheet. The vegetable parchments, greaseproof papers, Cellophanes, and thermoplastic films tested were not visibly affected by the high temperature storage.

Acknowledgments

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PACKAGING

VI. THE RELATIVE MERITS OF VARIOUS TYPES OF BAG CONSTRUCTION IN PRODUCING WATER-VAPOUR RESISTANT PACKAGES[1]

By C. G. Lavers[2]

Abstract

Water-vapour penetration was measured on pouch, flat, wedge, and square liner bags fabricated from Reynold's Metal A-51, 300 M.S.A.T. "Cellophane" coated 40 lb. per ream with a flexible wax composition, 55 lb. laminated bleached glassine, and 300 M.S.A.T. Cellophane. The bags were closed, where the material permitted, by heat-, glue-, and pressure-sealing, and by folding with or without tin-tie closures.

When Reynold's Metal A-51 or waxed Cellophane was used, excellent water-vapour resistance could be achieved with any of the bag types investigated, and a folded closure was as efficient as a heat-seal. With all materials except 300 M.S.A.T. Cellophane, bags made with glue were almost as good as those with heat-sealed construction. Unwaxed Cellophane or glassine provided more protection when the simpler forms of bags (pouch) were used. With unwaxed Cellophane, heat-sealing appeared to make a better liner than the use of glue, and a heat- or glue-sealed closure was superior to a double fold.

Introduction

An important factor in the packaging of many foods is the prevention of the passage of water-vapour either into or out of the package. Many flexible water-vapour barriers have been developed for this use. The water-vapour resistance of many of these barriers has already been assessed (1, 2), and it has been shown that, for products not likely to rupture the barrier, the best method of applying a water-vapour barrier is as a liner inside a carton (1). While the pouch type liner bag has generally been assumed to provide the greatest resistance to passage of water-vapour, little definite information is available on the relative merits of various types of bag construction. The purpose of this paper is to compare the water-vapour resistance of liner bags made in the basic commercial styles.

Materials and Methods

The names applied to various methods of forming bags are not constant from manufacturer to manufacturer, therefore the styles of bags tested and the names applied for the purpose of this study are illustrated in Fig. 1. The 'pouch' bag is the simplest to make, having only a seam at either side, and there is the least possible opportunity for water-vapour transmission through seams and seals. The 'flat' bag has two seams, one along the side, and another at the bottom; the junction of the side and bottom seams is a

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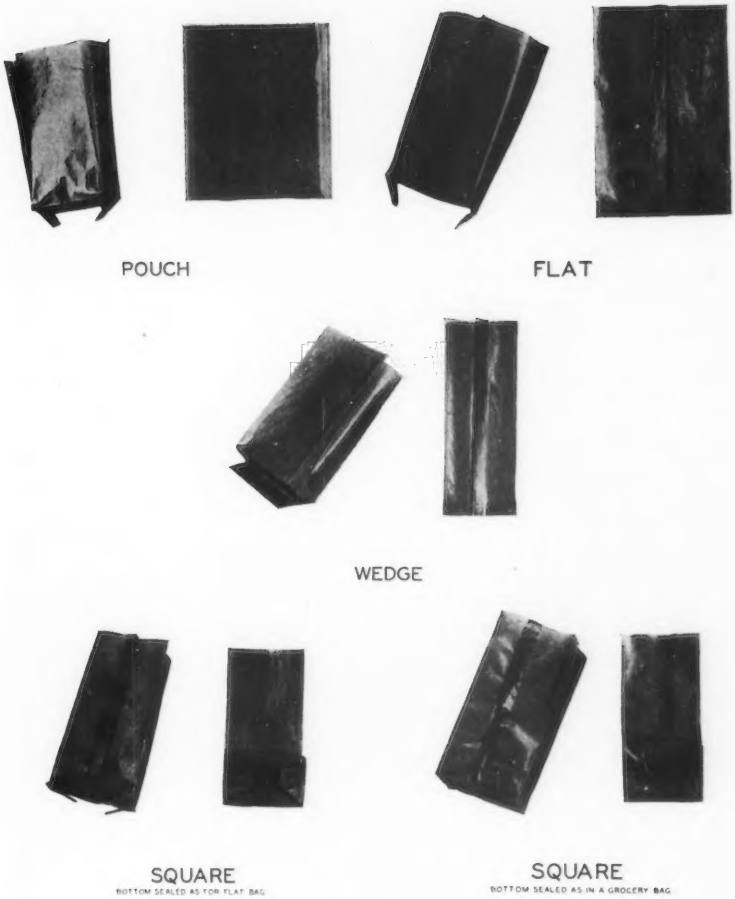

FIG. 1

FIG. 2

FIG. 1. *Construction of the various types of bags studied.*
FIG. 2. *Some methods of closing bags used in this study.*

possible point of entry for water vapour. The 'wedge' type bag shown in Fig. 1 has a single side seam, gussets, and a wedge closure (Fig. 2) at the bottom. The additional folds in this type of bag might be expected to cause higher rates of water-vapour transmission in it than in the previous types. Glue-sealed 'square', or self-opening bags, shown in Fig. 1, were made with both the common grocery bag style of bottom, and with a 'flat' seal (Fig. 2) on the bottom. The flat bottom seal should improve the water-vapour resistance of this type of bag over that of the wedge style of bag unless the material used is sensitive to the added creasing required to make it square when opened. Square bags made using heat-sealed construction were necessarily of the flat bottom closure style.

Besides the closures illustrated in Fig. 2, unsealed single and double fold closures, some with and some without a tin-tie were tested. When folded closures are used special care must be taken to see that the box is well filled so the top of the carton will prevent the fold from opening. In the course of the study, pressure sealed bags were also examined. Only heavily waxed material could be used for this purpose. All seams were heat-sealed except the final closure, which was made by running a dull pencil point across the mouth of the bag, causing the waxed surfaces to stick together.

Four materials with various characteristics were used to make the liners for this investigation. These were: Reynold's Metal A-51 (kraft paper laminated to metal foil coated with Butvar), 300 M.S.A.T. "Cellophane" coated 40 lb. per ream with a flexible wax composition, 55 lb. laminated bleached glassine (coated on one side with a heat sealing composition), and 300 M.S.A.T. Cellophane. When Reynold's Metal A-51 was used to make glue-sealed bags it was necessary to reverse the material and place the kraft on the inside of the bag and the heat-sealing surface outside.

The combinations of materials, bag styles, and closures tested are given in Table I.

The method of measuring water-vapour transmission was the same as that used in a previous investigation (1). The materials were fabricated into liners of suitable size to fit inside a light chipboard carton, 4 by $2\frac{3}{4}$ by $1\frac{5}{16}$ in. (opening end, $2\frac{3}{4}$ by $1\frac{15}{16}$ in.). The liner was opened, inserted into a carton, and partially filled with sawdust; then 73.5 gm. of anhydrous calcium chloride in a perforated P.T. Cellophane bag was added; this bag was surrounded by sawdust and the remainder of the liner was filled with sawdust; the liner and carton were then closed. Six filled packages were used to test each type of liner bag, and six packages without calcium chloride and sawdust were used to estimate the sorption of water-vapour by the packaging materials. The filled packages and dummies were placed in a cabinet operating at 95° F. and 100% relative humidity (vapour-pressure differential, approximately 42 mm. of mercury), and moisture gain was determined by weighing each package at weekly intervals for four weeks.

TABLE I

WATER-VAPOUR TRANSMISSION (GM. PER WEEK) OF VARIOUS TYPES OF LINER BAGS

(Standard error for mean transmission rates, 0.32 gm. per week)

Construction and type of bag	Closure	Packaging material			
		Reynold's Metal A-51	300 M.S.A.T. Cellophane coated 40 lb./ream wax composition	55 Lb. laminated bleached glassine, coated with a heat-sealing composition	300 M.S.A.T. Cello-phane
Glue-sealed	Glue-sealed				
Pouch	Flat	0.26	—	1.29	2.86
Flat	Flat	0.22	—	1.98	4.91
Wedge	Wedge	0.26	—	1.75	5.78
Square, bottom sealed as for flat bag	Wedge	0.22	—	2.25	3.74
Square, bottom sealed as in a grocery bag	Wedge	—	—	2.33	3.74
Heat-sealed	Heat-sealed				
Pouch	Flat	0.0	0.29	1.24	1.46
Flat	Flat	0.17	0.47	1.39	2.53
Wedge	Wedge	0.34	0.43	1.70	2.78
Square, bottom sealed as for flat bag	Flat	0.0	0.44	3.43	3.78
	Wedge	0.0	0.83	2.92	4.16
	Unsealed				
Pouch	Single fold, tin-tie	0.0	—	—	—
	Double fold, tin-tie	0.0	—	—	—
Square, bottom sealed as for flat bag	Double fold, flat	0.19	0.53	3.24	4.68
	Double fold, wedge	0.21	0.82	3.10	4.69
	Pressure sealed				
	Double fold, flat	—	0.60	—	—
	Double fold, wedge	—	0.56	—	—
	Single fold, flat	—	0.62	—	—

Results

Water-vapour transmission rates of the various types of bags tested are shown in Table I. These values were calculated by the method used in a previous study (1). The standard error for the mean transmission rates reported in the present study was of the same order of magnitude for all the different bag types. The average standard error was 0.32 gm. per week. For all types of bags the protection provided by the different materials in decreasing order of efficiency was: Reynold's Metal A-51, 300 M.S.A.T. Cellophane wax-coated 40 lb. per ream, 55 lb. laminated bleached glassine, and 300 M.S.A.T. Cellophane. This agrees with results obtained in a previous study (1).

The various types of liner bags made from Reynold's Metal A-51 did not differ significantly in behaviour. However, the transmission of glue-sealed bags was generally slightly higher than that of those made with heat-sealed construction, and the heat-sealed wedge bag appeared slightly inferior to the

other types. The water-vapour transmission of unsealed bags (folded closures), with or without a tin-tie, did not differ markedly from that of bags that were heat-sealed, but the addition of the tin-tie to a folded closure improved the water-vapour resistance somewhat.

Although no significant differences occurred in the water-vapour resistances of the various types of bags made of wax-coated Cellophane, the pouch type bag appeared to be slightly superior. Little difference in transmission was expected between types made with this material because the heavy wax coating when melted in the heat-sealing operation would flow into places around folds in the seal that might be left open when other materials are used. Unsealed folded closures were as good as those that received the added treatment of pressure sealing. This would probably not be true, however, if the fold was not held closed by the outer carton.

For any one type of bag little difference was noted between glue- and heat-sealed construction with liners made of laminated glassine. There was, however, a tendency for the efficiency of the bag to decrease as the complexity of construction increased, i.e., from pouch to flat to wedge to square. This was attributed to the combined effect of increased difficulty in sealing and the added folding of the material required in making the more complex bags. Glassine, being a relatively brittle material, develops pinholes easily when folded. Square, glue-sealed liners with the bottom sealed as in a grocery bag were as good as those with a flat seal on the bottom; and the water-vapour resistance of bags with a folded closure was equal to that of bags closed by heat-sealing.

Unlike the bags made of laminated glassine, heat-sealed Cellophane bags in the pouch, flat, and wedge styles were superior to those made with glue. This was probably due to the greater spring-back that occurs when Cellophane is folded. Cellophane is a very thin material, not readily creased, and it is difficult to obtain a perfect glue-seal (especially at corners) unless true surfaces are used to hold the material in place until such time as the glue has set. As with glassine, the more complex types of bags, whether heat- or glue-sealed, were generally less efficient water-vapour barriers. Equal protection was provided by square, glue-sealed bags with grocery or flat style bottoms. Folded closures on Cellophane bags were inferior to heat seals, likely because the thin springy nature of this material caused some opening of the fold even though the bags were well filled and held shut by the outer container.

Discussion

When the results in Table I are considered, it must be remembered that all bags were carefully made in the laboratory, and great care would be required to produce bags of equal quality on a commercial scale. For example, a square bag with a grocery type bottom as used in this experiment would be sealed more completely than the same product from most bag making machines at present in use. However, once the plant process has been perfected it

should be possible to make bags in any style superior to those used in this study. Nevertheless the results given here should represent the relative effectiveness of the various bag types, materials, and closures.

Fairly heavy materials, like Reynold's Metal A-51, and heavily waxed sheets (flexible wax composition) that are not sensitive to creasing can be formed into bags with high water-vapour resistance regardless of the type of bag used, and a folded closure can be as efficient as a heat-seal. However, materials that are sensitive to creasing, such as glassine, are best utilized for only the simpler types of bags. With materials like Reynold's Metal and glassine, bags sealed with glue are almost as good as those made with heat-sealed construction.

Thin springy materials, like unwaxed Cellophane, provide more water-vapour resistance when the simpler forms of bags (pouch) are used, and a heat- or glue-sealed closure is superior to a double fold. Heat-sealing rather than the use of glue appears to make a better liner with this packaging material.

The above results indicate that it is generally desirable to keep bag construction as simple as possible if the most protection from loss or gain of water vapour is to be expected. However, the bags of simple construction are often more difficult to use in small scale commercial or home operations. For these uses, the more complex bags may be satisfactory for packaging many products provided suitable materials are employed.

Acknowledgments

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DRIED MILK POWDER

VII. THE EFFECT OF SEASON OF PRODUCTION ON KEEPING QUALITY[1]

By Jesse A. Pearce[2] and W. A. Bryce[2]

Abstract

Milk powders of 1% butterfat content, produced in the fall of the year, had higher initial palatability scores than similar powders prepared in the spring. The skim milk powders from fall milk decreased in quality throughout a storage period of 16 wk. at temperatures of 80°, 100°, or 120° F. Similar powders from spring milk stored at 80° F. increased in quality throughout the storage period while those stored at 100° and 120° F. first increased and then decreased in quality. Powders of 26 or 28% butterfat, produced in the spring or in the fall, had equal initial palatability scores and when stored deteriorated equally. Fall milk powder containing 30% butterfat was better initially than the comparable spring sample, but, when stored, quality changes in both types were about equal. At each storage temperature all whole milk powders deteriorated at about the same rate.

Introduction

In conjunction with investigations of some of the factors affecting deterioration of milk powder, e.g., cooling subsequent to drying (5), exposure to light (6), storage temperature (1), method of packing (7, 11), moisture content (1), and producer (1), it was deemed advisable to evaluate the difference in the behaviour of milk powder produced at different seasons of the year.

It has been shown that liquid milk obtained during the fall and winter months has a higher solids content than spring and summer milk (2, pp. 29-31; 4, p. 405; 10, pp. 55-61), that spring milk is poorest in fat and fall milk the richest (2, 10) and that the fat of milk produced in the fall of the year, when good pasture is no longer available, has a lower iodine value than the fat of spring milk (3). It would be expected, therefore, that fall milk, when dried, would be more stable than powder produced in the spring. This paper describes the results of a storage study on samples of spring and fall milk powders of different fat levels but of equal moisture contents.

Materials and Methods

The spring and fall milk powders used in this experiment were spray-dried and were produced during the latter part of May and early in December, 1944. The butterfat levels compared were 1, 26, 28, and 30%. The moisture content of the powders was adjusted to 2% before packing in tin-plate containers with air as the headspace gas. The palatability of the powders was determined initially and after 2, 4, 8, and 16 wk. storage periods at temperatures of 80°,

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100°, and 120° F. (27°, 38°, and 49° C.). In assessing the quality of the powders, samples were reconstituted as previously described (5) and palatability was assessed by 14 tasters. Scoring was done on a scale of 10 (the equivalent of excellent fresh whole or skim milk) to 0 (a repulsive specimen). A score of 4 is usually considered the point at which milk powder is no longer suitable for use as a milk drink. The reliability of the scoring by the taste panel has been estimated and palatability assessment was found to be more suitable than any of the chemical tests of milk powder quality (5).

Results

The data for the 4, 8, and 16 wk. samplings were assessed by an analysis of variance with the results shown in Table I. This table shows that no constant difference could be attributed to the use of either spring or fall milk in powder production. The difference between samples was attributed to the inclusion

TABLE I

ANALYSIS OF VARIANCE OF PALATABILITY DATA ON STORED POWDERS PREPARED FROM SPRING AND FALL MILK

Variance attributable to:	Degrees of Freedom	Mean square
Seasons	1	1.15
Samples	3	1.12*
Temperature	2	15.30**
Storage time	2	11.93**
Seasons × samples	3	2.45**
Seasons × temperature	2	1.45*
Seasons × time	2	3.83**
Samples × temperature	6	0.25
Samples × time	6	0.83*
Temperature × time	4	1.28*
Residual	40	0.35

* *Exceeds the 5% level of statistical significance.*
** *Exceeds the 1% level of statistical significance.*

of data for skim milk powder in the comparison. Skim milk powders are generally considered to be of poorer quality, when reconstituted as a milk drink, than whole milk powders. The significant effects of storage temperature and storage time have been discussed in earlier papers, and the other factors of significance can be explained by referring to Fig. 1.

As shown in Fig. 1, skim milk powder (1% fat) from fall milk had a higher initial palatability than skim milk powder from spring milk but decreased in palatability during storage at all temperatures, while the palatability score of skim milk powders from spring milk first increased, then decreased during storage at 100° and 120° F., but at 80° F. increased throughout the storage period. It is of interest to note that in previous studies, all skim milk samples exhibiting low initial palatability and increasing palatability during storage

have been produced in the spring of the year (5, 6, 7) while the only other general decrease similar to that observed in this study was in a powder produced from fall milk (6). The possibility that this difference in behaviour was attributable to plant practice seems unlikely since powders produced in the spring by two different companies exhibited parallel behaviour (1).

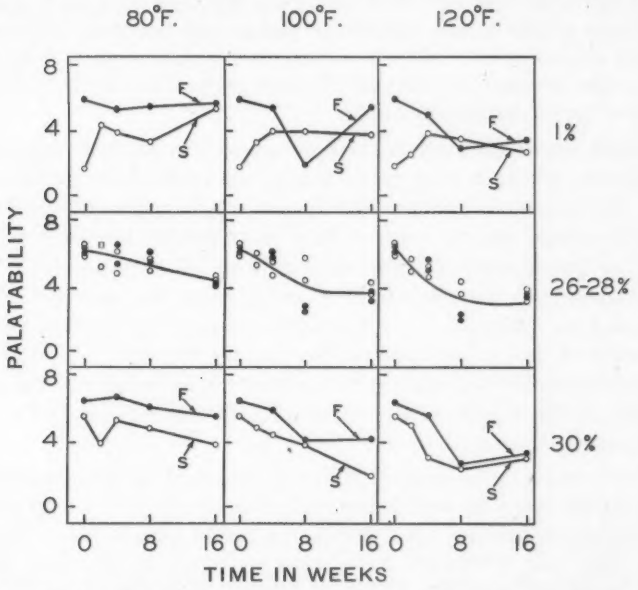

FIG. 1. *The decrease in palatability of stored milk powders prepared from spring and fall milk.*

Whole milk powders having 26 or 28% fat, and prepared from milk produced in the spring or in the fall, did not differ from each other in keeping quality. However, fall milk powder with 30% butterfat had a higher initial palatability than the comparable spring sample. The high-fat, spring powder had a lower palatability than any of the other whole milk powders. This difference may be attributable to some variation in plant practice. Deterioration in both 30% butterfat powders occurred at about the same rate. Deterioration in all whole milk powders showed comparable trends at the same storage temperatures. Changes in whole milk powders were different from those in the skim milk powder from spring milk, but were similar to, although slightly more rapid than, the changes in skim milk powder from fall milk.

Discussion

Experimental work on milk in Finland (10) has shown an increase in fat and protein of milk produced during the summer months and an increase in lactose of that produced during the winter months. Since the change in

composition of milk as cows go to pasture, and vice versa, is not abrupt, it might be expected that the lactose–protein ratio in May would be higher than the ratio in December milk. Calculations on American data (6) show that, for Jersey cows, the ratio of lactose to protein in May is 1.42 compared with about 1.15 for November and December. This makes a difference of 2.5 to 3% in the lactose content of spring and fall dried whole milk and about 4% difference in the lactose content of spring and fall skim milk powders. This, when considered in relation to the high drying temperatures used in preparing skim powders, makes possible some explanation of the difference in behaviour of spring and fall skim milk.

It has been shown that the addition of lactose to a partially defatted milk prior to drying provided some protection to the product during storage (8). However, it is known that lactose deteriorates rapidly when subjected to heat. Spring milk powder might, therefore, have more volatile breakdown products from lactose decomposition during drying than fall milk powder. As suggested previously (6), these degradation products may be dissipated as a result of the repacking operation or of chemical recombination during storage to form substances that do not possess disagreeable flavours. As storage proceeds, the undesirable degradation products would diminish and the preservative effect of the higher lactose content of the spring skim milk powder would become noticeable.

Milk fat from cattle on pasture differs in degree of unsaturation from the fat of milk from partially stall-fed animals (4). If the milks used here conformed in unsaturation to English milks, it would be expected that the butterfat in the fall milk would have an iodine value about six lower than the butterfat in the spring milk. Fall milk powder, then, should be more stable than spring milk powder. Some reflection of this increased stability may have been shown by the higher palatability of the fall milk powder containing 30% fat. However, the deterioration noted in powders of 26 and 28% fat contradicted this and indicated that the butterfat at both seasons was equally susceptible to deterioration.

The facts that packing in inert gases affords only partial protection to whole milk powder (7), that light exerts a harmful effect on skim milk powder (7), and that almost equal deterioration occurred in some whole and skim milk powders point to solids-not-fat as an important factor in milk powder deterioration. The observation that milk powders containing 50 to 55% fat keep 15 to 18 months while powders with 5 to 6% keep only about four months (9) supports this assumption.

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PRESERVATION OF EGGS

V. METHODS FOR DETERMINING YOLK INDEX[1]

By N. E. Gibbons[2]

Abstract

Breaking out the egg on a glass plate and measuring the height and width of the yolk in position in the white is a rapid and easy method of determining yolk index. The correlation coefficient between this method and one of the more laborious methods, in which the white is removed, is .97. The prediction equation is $y = -0.001 + 0.9172x$.

Introduction

The use of the yolk index as a measure of egg quality was first proposed by Sharp and Powell (3). In their method, the yolk was completely freed of all the white. To remove the last traces of adhering albumen, the yolk was held in the palm of the hand and wiped gently with a cloth. It was then placed on a glass plate, the diameter and height measured, and the yolk index calculated by dividing the latter value by the former. After being placed on the glass plate the yolk continued to flatten for a considerable length of time, but this flattening was most rapid during the first 60 min. However, it was possible to obtain reasonably accurate information if the measurements were made after the yolk had been standing for five minutes. When determining the yolk index by this method, the chances of breaking the yolk are obviously high, especially when storage eggs are used.

The method was modified by Smith (4, pp. 60-61) who left the adherent film of white. This involved less handling and less risk of damage. It was also suggested that the value obtained with the white adhering was of more interest as a basis for judgment of quality. A standard period of two minutes was allowed to elapse before measurements were made.

Further modifications were made at the Low Temperature Research Station at Cambridge (1). As, in this study, comparisons were made with this method it is given in detail: the shell is cracked round by means of a knife or scalpel and the contents carefully transferred to an egg separator. As soon as the major portion of the thick fraction of the white has passed through the opening of the separator, the yolk is allowed to slide into a glass dish containing a sugar solution isotonic with the yolk, i.e., 10.4 gm. of sucrose per 100 gm. of water. While in this sucrose solution the remainder of the thick white and chalazae are removed. The yolk is then placed on a level glass plate, covered with a small beaker or crystallizing dish and allowed to

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settle for three minutes. The height of the yolk is then determined with a depth micrometer and the width measured across the long and short axes. The index is expressed as the height divided by the mean width.

In the N.R.C. laboratories it has been the practice to break out the egg onto a glass plate and measure the height and width of the yolk as it rests on the white (2). Practically the yolk is never considered without the white and as the support given by the albumen lessens with time, as does the strength of the yolk membrane, it seems reasonable to measure the yolk in this position. Furthermore the above methods are time-consuming and too often considerable time and material are wasted because the yolk breaks at the last moment. To test the validity of the N.R.C. method a comparison was made between it and the method used at the Low Temperature Research Station.

The N.R.C. method is as follows. The egg is broken out onto a clean level glass plate and the yolk diameter measured immediately with calipers along the axis bisecting the short and long diameters. The yolk height is then measured with a spherometer. These two measurements are completed within 30 to 40 sec. of breaking the egg.

Experimental

For comparison, the yolk indices of 182 eggs of various grades and storage histories were determined first by the N.R.C. method and then by the L.T.R.S. method. The scatter diagram and regression line are shown in Fig. 1. The

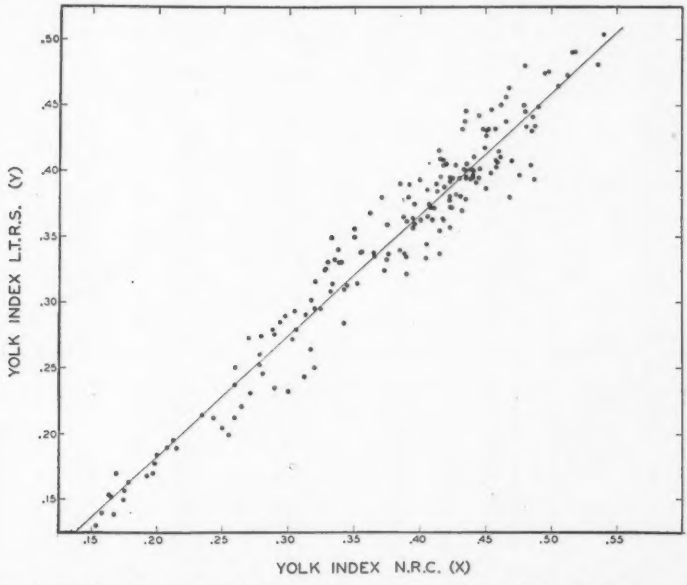

FIG. 1. *Relation between yolk indices determined by N.R.C. method and the method used by Low Temperature Research Station.*

correlation coefficient between the two sets of values is .97. The prediction equation is $y = -0.001 + 0.9172x$. The N.R.C. method therefore gives practically the same results as the longer method, and the losses from breakage are negligible.

As may be seen from the regression line the present method gives slightly higher values than the L.T.R.S. method. The white under the yolk contributes slightly to this but the effect decreases as the white thins (Table I). This was shown by breaking the eggs out on a cold brass plate, taking the

TABLE I

EFFECT OF AMOUNT OF WHITE UNDER YOLK ON YOLK INDEX WHEN MEASURED BY N.R.C. METHOD

——	Yolk diameter, in.	Yolk height, in.	Yolk index	Height of white under yolk, in.	Corrected yolk height, in.	Corrected yolk index
Fresh eggs	1.67	.840	.503	.028	.812	.486
	1.68	.780	.464	.017	.763	.454
	1.74	.870	.500	.030	.840	.483
	1.69	.775	.458	.030	.745	.441
	1.70	.730	.429	.031	.699	.411
	1.78	.792	.444	.020	.772	.434
	1.65	.798	.484	.032	.766	.464
	1.69	.877	.519	.038	.839	.496
	1.64	.765	.466	.035	.730	.445
	1.62	.869	.536	.025	.844	.521
Average	1.69	.810	.480	.029	.781	.464
Commercial Grade *C*	1.63	.695	.430	.025	.670	.411
	1.67	.721	.432	.040	.681	.407
	1.71	.752	.440	.025	.727	.425
	1.82	.645	.354	.018	.627	.344
	1.61	.686	.426	.007	.679	.422
	1.70	.679	.399	.024	.655	.385
	1.69	.783	.463	.029	.754	.446
	1.82	.815	.448	.040	.775	.426
	1.68	.695	.414	.022	.673	.401
	1.65	.722	.438	.031	.691	.419
Average	1.70	.719	.424	.026	.693	.409
Experimental eggs stored at 70° F.	1.98	.397	.201	.002	.395	.199
	1.82	.585	.321	.011	.574	.315
	1.70	.631	.371	.008	.623	.366
	1.89	.540	.285	.011	.529	.280
	1.76	.602	.342	.001	.601	.341
	1.77	.571	.322	.006	.565	.319
	1.81	.512	.283	.001	.511	.282
	1.78	.605	.340	.006	.599	.336
	1.78	.535	.300	.003	.532	.299
	1.80	.617	.343	.017	.600	.333
Average	1.81	.560	.311	.007	.553	.307

usual measurements, and then placing the plate over a steam jet. The albumen was quickly coagulated, the yolk removed, and the thickness of the albumen measured.

The flattening of the yolk due to the removal of the supporting albumen should also reduce the yolk index. The differences in yolk index of 60 eggs, as determined by the two methods, ranged from 0.066 to 0.020, and this flattening may contribute the greater part of the difference. The effect of both the white under the yolk and the removal of the supporting albumen decreases as the quality of the egg decreases. This is evident from the slope of the regression line.

Acknowledgments

The assistance of Ursula Irish and Ruth Michael in making many of the measurements and computations is gratefully acknowledged.

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THE EFFECT OF METHOD OF COOKING ON THE MOISTURE CONTENT OF CANNED PRE-COOKED POULTRY MEAT[1]

By D. MacDougall[2] and N. E. Gibbons[3]

Abstract

Moisture content of the meat and solid content of the broth from open- and pressure-cooked chicken and fowl were investigated during cooking and subsequent processing. During cooking, pressure-cooked meat lost more moisture than open-cooked meat, but during canning and separating the reverse was true. For these reasons, approximately 4 oz. of open-cooked meat, as compared with 3.6 oz. of pressure-cooked meat, must be canned to obtain 3.5 oz. of meat in the finished product. During cooking there was a greater loss of moisture from dark than from light meat. Under all the cooking conditions used the loss of weight from fowl during processing and separation was greater than that from chicken meat. The loss in weight of meat during canning and processing is mainly due to moisture changes rather than the loss of solids.

Introduction

Canadian regulations (1) state that canned poultry to be sold as 'jellied pack' must have a solid meat content of not more than 55% and not less than 50% of the final pack. Poultry canners who used the open-cook method were originally led to believe that, if $3\frac{1}{2}$ oz. of solid meat were to be obtained from a 7-oz. can after retorting and separating, it was necessary to place $3\frac{3}{4}$ oz. of cooked meat in the can. Both canners and poultry inspectors found that the loss of weight with open-cooked meat was greater than allowed for by the above limits. On the other hand with pressure-cooked meat there was little difficulty in meeting the requirements. Therefore, it was decided to investigate the moisture relations of poultry meat throughout the usual canning operation. Both chicken and fowl were studied and the light and dark meat were treated separately. Moisture content of the meat and solid content of the broth before and after the various heat treatments involved were investigated.

Experimental Procedure

Moisture was determined by cutting a sample of meat into a weighed aluminum drying dish, placing this in an air oven at 100° C. for two hours, and finally drying to constant weight *in vacuo* at 100° C. A period of 16 hr. in the vacuum oven was shown to be sufficient time for samples to reach constant weight and therefore this drying time was used throughout the experiment. The solid content of the broth was determined by drying the sample to constant weight in a small beaker in the air oven at 100° C.

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To investigate sampling technique, the moisture content of various muscles of dressed chickens was determined. The pectoral, leg, and wing muscles were dissected from two birds and their moisture contents were recorded. It was concluded (Table I) that the moisture content of a single muscle or a portion of a muscle, on either side, could be used as an index of the moisture content of the meat of a whole bird.

TABLE I

MOISTURE CONTENT OF VARIOUS MUSCLES OF DRESSED CHICKEN

Chicken	Muscle	Moisture, %	
		Left	Right
A	Outer pectoral	74.0	74.3
	Inner pectoral	73.5	73.9
	Wing	74.5	74.5
	Leg	74.4	74.1
B	Outer pectoral	72.8	72.7
	Inner pectoral	72.8	72.6
	Wing	73.3	73.4
	Leg	71.4	71.0

In the main experiment, three open and three pressure cooks, using four birds in each, were carried out on both chicken and fowl, which were cooked separately. The open cooks were made in a steam-jacketed kettle with the steam outlet from the central chamber open, giving an internal temperature of 100° C. (212° F.). In these cooks approximately one litre of water was used for each 5 lb. of bird. The times were 50, 75, and 100 min. The pressure cooks were done in the same kettle for 20, 30, and 40 min. at 121° C. (250° F., 15 lb. steam pressure). The times were chosen in each case to give under-, normal-, and overcooked meat. Before cooking, all birds were tagged and a portion of the outer pectoral muscle was removed to determine the moisture content of the light meat and a portion of either the gastrocnemius or biceps femoris muscle was taken for the moisture determination of the dark meat. After cooking, portions of the corresponding muscles on the opposite side of each bird were removed and their moisture contents determined.

After sampling, the cooked meat was stripped from the bones and 3½-oz. portions were weighed into 7-oz. cans. Light and dark meat were canned separately. The broth from each cook was defatted, adjusted to a sp. gr. of 1.000 and 1.010 at 50° C. (122° F.) for open- and pressure-cooked meats, respectively, and 2.0% Irish moss gelose was added as a jelling agent along with 4% salt according to the regulations for the packing, grading, and marking of canned poultry (1). When broth samples had been taken for solids determinations, 3½-oz. portions of broth were poured over the meat and the cans were preheated and sealed. All cans were retorted for one hour at 116° C. (240° F.).

Two types of separation apparatus were available, the type described by Reedman (2) and a modification of this apparatus (Fig. 1) designed by Mr. T. A. Steeves, formerly of these laboratories. The rate of heat penetration

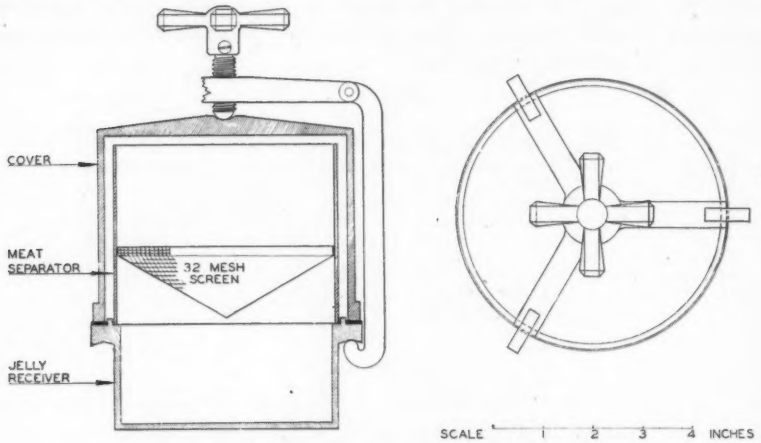

FIG. 1. *Modified separation apparatus for canned poultry.*

into the apparatus was determined using copper–constantan thermocouples. A period of 30 to 40 min. in the autoclave was necessary to raise the meat and jelly inside the separator to 100° C. Accordingly, all separations were made at 121° C. for 45 min. To compare the efficacy of the two types of apparatus, duplicate sets of canned chicken were run in each type.

Since some of the loss of moisture was attributed to the method of separating the meat and jelly, an attempt was made to determine the actual moisture loss due to the separation procedure. However, since it was not possible to separate the meat and jelly completely by means other than heat, no conclusive results were obtained.

Since it is commercial practice in open cooking to cover the birds completely with water and to do several cooks in the same broth, the experiment was repeated in this way. All determinations were carried out as before and, in order to have a valid check, pressure cooks were carried out on birds obtained from the same source. In the open cooks it was necessary to add eight litres of water to cover four birds completely. This was brought back up to volume after each cook. Agar (1%) was used as the gelling agent in this test.

All results were subjected to statistical analysis.

Results

Moisture Changes in Meat

Average moisture losses from chicken and fowl during cooking and the canning and separation procedures are shown in Table II. Necessary differ-

TABLE II

LOSS OF ORIGINAL MOISTURE FROM POULTRY MEAT DURING COOKING AND CANNING

Treatment	Average percentage loss during cooking	Average percentage loss due to cooking, and to canning and separating	Average percentage loss due to canning and separating
Chicken			
Open cook			
50 min.	13.9*	16.5	2.6
75 min.	17.4	17.4	0.0
100 min.	14.1	16.6	2.5
Pressure cook			
20 min.	19.9	21.6	1.7
30 min.	18.8	18.9	0.1
40 min.	21.6	21.4	−0.2
Necessary difference (5%)	2.5	1.8	3.1
Fowl			
Open cook			
50 min.	12.1**	20.0	7.9
75 min.	13.8	18.3	4.5
100 min.	14.4	17.8	3.4
Pressure cook			
20 min.	18.7	19.0	0.3
30 min.	19.8	19.2	−0.6
40 min.	18.8	17.7	−1.1
Necessary difference (5%)	1.4	2.6	2.9

* *Means of 16 observations.*
** *Means of 8 observations.*

ences for a 5% level of significance are also given. Moisture losses are calculated throughout on the basis of the original weight of raw meat.

These results show that pressure cooking removes a significantly greater amount of the original moisture from both chicken and fowl meat than does open cooking. The only significant effect of time of cooking noted was with the short time open cook on fowl. Here the loss of moisture was significantly less than for either of the longer cooks.

The data obtained with chicken meat after separation show the same general effects as those obtained after cooking; the total moisture loss was significantly greater from the pressure-cooked than from the open-cooked meat. However, the loss due to canning and separating was greater for the open than for pressure-cooked meat, but time of cooking had little effect. Canning and separation after pressure cooking caused the greatest loss in meat that was cooked for 20 min. only. With the fowl meat, canning and separation eliminated any difference in moisture due to method of cooking since the moisture loss attributable to canning and separation was much greater in the

open- than the pressure-cooked meat and in each instance was inversely proportional to the time of cooking. There are indications that after canning, over-cooked meat may reabsorb some moisture.

The percentage losses of original moisture from both light and dark meat are compared in Table III. It is evident that dark meat lost significantly

TABLE III

PERCENTAGE OF ORIGINAL MOISTURE LOST FROM LIGHT AND DARK CHICKEN MEAT DURING COOKING AND PROCESSING

(Means of 12 observations)

Treatment	Type of meat	Percentage loss of original moisture during cooking	Percentage loss of original moisture after separation	
			Old separator	New separator
Open cook	Light	11.2	15.7	13.5
	Dark	19.1	19.8	18.4
Pressure cook	Light	18.5	19.9	18.2
	Dark	21.7	22.6	21.8
Necessary difference (5%)		2.5	1.4	1.4

more moisture than light meat, the difference being greater in open than in pressure cooking. These differences persisted even after processing and separation. Although the results are not presented, similar differences were noted with fowl meat.

Comparison of the results obtained with the two types of separation apparatus show that the older type dried out the meat considerably more than did the newer one.

TABLE IV

WEIGHT OF MEAT OBTAINED AFTER SEPARATION (ORIGINAL WEIGHTS, 3.50 OZ.)

Treatment	Chicken, oz.	Fowl, oz.
Open cook		
50 min.	3.05*	2.67**
75 min.	3.06	2.88
100 min.	3.16	3.04
Pressure cook		
20 min.	3.27	3.10
30 min.	3.44	3.37
40 min.	3.46	3.29
Necessary difference (5%)	0.17	0.17

* *Means of 16 observations.*

** *Means of 8 observations.*

The average weights of meat obtained after separation are contained in Table IV. These results confirm those obtained in the moisture studies. It will be noted that method has a much greater effect than time of cooking on the weight of meat obtained. In addition, the loss from fowl meat was greater than that from chicken meat for all cooking conditions. There were no significant effects of cooking time with the open-cooked chicken. With pressure-cooked chicken the loss from meat cooked 20 min. was greater than from meat cooked for the longer times. This difference just reaches the 5% level of significance. There was a significantly greater loss of weight from the fowl cooked 20 min. than from fowl that received the longer cooks and that had been dehydrated to a greater extent during the cooking process. It should also be mentioned that there was a significant difference between the weights of light and dark meat obtained after separation from fowl but not from chicken.

As the changes in percentage of solid material in the broth after canning and separating were relatively small and there were no significant differences between cooks, these results have not been included. However, it should be

TABLE V

LOSS IN WEIGHT (OZ.) FROM CANNED CHICKEN AND FOWL DURING CANNING AND SEPARATING, TOGETHER WITH ESTIMATES OF THE WEIGHT OF COOKED MEAT NEEDED TO OBTAIN 3½ OZ. AFTER CANNING AND SEPARATING

Treatment	Average moisture loss	Average solids loss	Combined loss	Total observed loss	Calculated weight to obtain 3.5 oz. after canning and separation
Chicken					
Open cook					
50 min.	0.34	0.07	0.41	0.45*	4.0
75 min.	0.26	0.08	0.34	0.44	4.0
100 min.	0.28	0.03	0.31	0.34	3.9
Pressure cook					
20 min.	0.18	0.07	0.25	0.23	3.7
30 min.	0.04	0.05	0.09	0.06	3.6
40 min.	0.02	0.05	0.07	0.04	3.5
Fowl					
Open cook					
50 min.	0.71	0.14	0.85	0.83**	4.6
75 min.	0.48	0.14	0.62	0.62	4.3
100 min.	0.36	0.13	0.49	0.46	4.0
Pressure cook					
20 min.	0.27	0.13	0.40	0.40	4.0
30 min.	0.12	0.01	0.13	0.13	3.6
40 min.	0.16	0.06	0.22	0.21	3.6

* *Means of 16 observations.*

** *Means of 8 observations.*

noted that there was a greater, but not significant, loss of solid material to the broth from dark than from light meat.

The entire experiment is summarized in Table V. In this the average losses of both moisture and solids are presented together with the total observed loss in weight. In calculating the loss of solid material to the broth it was assumed that the dry weight lost by the meat in the canning and separation processes was gained by the broth. The principal loss of weight was due to moisture and not to solid material. The contrast between the results for chicken and those for fowl should be especially noted. For every cooking condition used the meat obtained from fowl showed a greater decrease in weight on subsequent processing than did that obtained from chicken. It can be seen from these results that if a can of chicken that has been open cooked is to contain 50% by weight of meat after separation, it must contain about 60% of meat initially. The final column of Table V gives an estimate of the weights of precooked meat that must be canned if $3\frac{1}{2}$ oz. are to be obtained after autoclaving and separation.

Acknowledgments

The authors are indebted to Mrs. R. Michael, Mrs. U. Irish, Mr. John Francis, and Miss Edna Birchard for technical assistance and to Mr. T. A Steeves for permission to include the design of the separation apparatus.

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PRECISION OF ASSESSMENT OF PALATABILITY OF FOODSTUFFS BY LABORATORY PANELS

II. SALTINESS OF BACON[1]

By J. W. Hopkins[2]

Abstract

Numerical ratings of the salty taste of freshly cooked portions of 80 pieces of Wiltshire-cured Canadian bacon by each member of a panel of 23 judges are analysed statistically, with results in general qualitative agreement with those previously reported for other palatability tests made in the same laboratory. Single assessments were subject to considerable random variation superimposed upon wide differences between individuals in respect of both tolerance and sensitivity. Nevertheless, a significant element of correlation made possible reproducible results, although it is calculated that to discriminate differences of the order of 5% on the organoleptic scale would have required 35 and 62 judges for intra- and inter-panel comparisons, respectively. The preferred degree of saltiness corresponded to a sodium chloride content of the cooked bacon of about 4¼% in the absence, and of roughly 4% in the presence of 2½ parts per thousand of sodium nitrate.

Introduction

In an earlier paper (3) the writer distinguished between 'grading' (absolute) and 'analytical' (relative) assessments of the palatability of foodstuffs by panels of judges, and described the results of statistical analyses of ratings of butter, dried eggs, dried milk, and ration biscuits made in these laboratories. These analyses included a numerical investigation of the judging characteristics of individuals by computation of the correlation coefficients and regression equations relating their assessments to the average of those of all other members of the same panels. A parallel study has since been made of assessments of the saltiness of cooked bacon, the outcome of which is reported now.

Data

Data for this study consisted of numerical ratings of the saltiness of freshly cooked portions of 80 different pieces of Wiltshire-cured Canadian bacon by each member of a panel of 23 judges, 17 male and 6 female, recruited from the scientific, technical, and administrative staff of the Divisional laboratories. Chemical analysis of samples of the cooked material indicated contents of sodium chloride ranging from about 4½ to 9%, of sodium nitrate from 1/20 to ½%, and of sodium nitrite from 15 to 55 parts per million. Each judge tasted samples from all 80 pieces in groups of four and at the rate of eight per day. Subjective appraisals of saltiness were expressed numerically in accordance with the convention currently adopted in these laboratories. In this, which

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[2] *Biometrician.*

differs from the one previously used (3), zero represents the ideal in the estimation of the judge, and excess or deficiency of the flavour in question is rated on an integral scale of + 5 to − 5.

Results

An analysis of the variance (2) of the 1840 foregoing individual assessments gave mean squares of 54.743 between judges (averaged over all samples), of 11.783 between pieces (averaged over all judges), and of 1.133 for the residual fluctuations of individual ratings. The standard deviation of an average rating appropriate to intra-panel comparisons of pieces was thus $\sqrt{1.133/23}$, i.e., ± 0.22. To attain the 5% level of statistical significance therefore, a difference in the average ratings of two pieces would have to be at least $1.96\sqrt{2 \times 1.133/23}$, namely, ± 0.61. To reduce this 'necessary difference' to ± 0.50 would have required a panel of 35 judges.

From the mean squares listed in the preceding paragraph the underlying 'population variance' of judges' averages may be estimated (1) at (54.743 − 1.133)/80, corresponding to a standard deviation of ± 0.82, although this figure, which involves one component based on only 22 degrees of freedom, is subject to correspondingly more uncertainty than that for the residual variance, for which 1738 degrees of freedom were available. From this estimate, therefore, it would have to be inferred that to be regarded as statistically significant at the 5% level, a difference in average ratings of samples assessed by two separate panels of the same size and variability as the one here considered would have to amount to at least $2.069\sqrt{2 \times (0.6701 + 1.133)/23}$ i.e., to ± 0.82. Panels of the order of 60 members each would therefore be estimated as required to reduce this inter-panel necessary difference to ± 0.50. If each judge made two independent assessments of samples from the same piece, this number would be reduced to rather more than 40, but only at the cost of increasing the total number of man-hours devoted to assessment in the ratio of about 85 to 60, as well as of entailing a corresponding increase in the quantity of test material and in the labour of preparation.

As in all the four cases previously considered, there were pronounced differences in personal preference, the average assessment of the saltiness of all 80 pieces by individual judges ranging from + 3.24 to − 0.54, i.e., from considerably over to slightly under the desired amount. The average assessment by the panel as a whole was + 1.20. Table I shows the deviation of the average for each judge from that of the remainder of the panel, and also lists the correlation and regression coefficients relating the assessment of single samples by each judge to the average assessment of samples of the same piece by the rest of the panel. As the average numerical assessment of the various pieces ranged only from + 2.70 to − 1.13, while the irregular fluctuation of single assessments has already been noted as giving rise to a mean square deviation of 1.133, generally high coefficients of correlation of individual with group assessments could not be expected. In fact the highest obtained was

TABLE I

STATISTICAL CHARACTERISTICS OF INDIVIDUAL JUDGES' ASSESSMENTS

Judge	Average deviation from mean of all others	Coefficient of correlation with means of all others	Coefficient of regression on means of all others
No. 1 (male)	− 0.08	.57***	0.85
No. 2 (female)	− 0.31	.59***	1.32
No. 3 (male)	− 0.53	.63***	0.78
No. 4 (male)	− 0.26	.45***	0.39
No. 5 (male)	+ 0.89	.57***	0.90
No. 6 (male)	+ 0.84	.69***	1.06
No. 7 (male)	+ 1.07	.33**	0.52
No. 8 (female)	− 0.38	.41***	0.69
No. 9 (male)	− 0.89	.11	0.02
No. 10 (female)	+ 0.20	.56***	0.89
No. 11 (male)	+ 0.97	.70***	1.72
No. 12 (female)	− 0.12	.64***	0.82
No. 13 (male)	− 0.33	.51***	0.55
No. 14 (female)	− 1.06	.47***	0.60
No. 15 (male)	+ 0.45	.64***	0.92
No. 16 (male)	− 0.02	.66***	1.52
No. 17 (female)	− 0.47	.46***	0.64
No. 18 (male)	+ 0.26	.62***	1.18
No. 19 (male)	+ 2.13	.43***	0.93
No. 20 (male)	− 0.17	.70***	1.18
No. 21 (male)	− 1.11	.15	0.37
No. 22 (male)	− 1.82	.32**	0.59
No. 23 (male)	+ 0.78	.62***	1.24

** *Attains 1% level of statistical significance.*
*** *Attains 0.1% level of statistical significance.*

0.70. However, eight of the judges had coefficients in excess of 0.60, which in the circumstances are regarded as reasonably satisfactory, and those of only two were not statistically significant.

The range of individual sensitivity indicated by the regression coefficients of Table I is greater than that provided by the previously reported (3) assessments of over-all palatability. Judge No. 20, with an average deviation from the mean of all others of only − 0.17 unit, a correlation coefficient of 0.70, and a regression coefficient of 1.18, conformed most closely to the average reaction of the group as a whole. No. 11, who had an average deviation of + 0.97 and correlation and regression coefficients of 0.70 and 1.72 was the most sensitive to variations in saltiness, to which on the other hand Nos. 9 and 21 appeared to be very largely (the former almost completely) indifferent. Nos. 19 and 22, with average deviations from the mean of all other judges' assessments of + 2.13 and − 1.82, respectively, provided the individual extremes of aversion to and tolerance for saltiness. All the individuals specified were males, but the results as a whole were not indicative of any statistically significant average difference between the sexes in respect of either tolerance or sensitivity.

The present results differ from the majority of organoleptic assessments in that they may be appropriately related to specific chemical constituents of the cooked meat, and in this way it was found that the coefficients of partial correlation of the average assessment and the sodium chloride and nitrate contents reported for the various pieces were + 0.62 and 0.25, respectively, the latter attaining the 5% level of statistical significance. The small variations in sodium nitrite recorded were without demonstrable effect on the assessment. It would be unjust to attribute the moderate level of even the first of these correlation coefficients entirely to inconsistency of the judges or masking effects of other flavours, as it was evident that the chemical determinations were themselves subject to appreciable sampling discrepancies.

The average assessment for each piece obtained from the panel as a whole was related to sodium chloride and nitrate content by the regression equation of least squares:

$$\textit{Assessment} = -1.78 + 0.375\ (\textit{NaCl per cent}) + 0.090\ (\textit{NaNO}_3\ \textit{per mille}) \pm 0.45.$$

As no significant reduction of the residual variance resulted from inclusion of the quadratic term in NaCl, it was inferred that the relation was sensibly linear over the range considered.

Owing to its rather limited range of saltiness, the present series of observations is not very informative in respect of the variance of individual assessments at different average preference levels. The inter-judge standard deviations for all samples receiving average assessments between 0 and 1, between 1 and 2 and between 2 and 3 were $\pm$ 1.29, $\pm$ 1.18, and $\pm$ 1.43, respectively. The last of these is significantly larger than either of the other two, and thus provides some indication of slightly greater divergence in the assessment of moderately unpalatable samples. Additional data are, however, required to investigate this point adequately.

Conclusions

These results for the specific attribute of saltiness of bacon are in qualitative agreement in four respects with those already reported (3) for general palatability of certain other foodstuffs. First, they indicate that single assessments by unselected judges were characterized by considerable random variation but also by a demonstrable element of correlation, making possible reproducible differentiation between samples by a panel of adequate size. Second, they again provide evidence of persistent differences in the preference level of individuals, necessitating substantially more judges for a specified degree of reproducibility in inter- than in intra-panel comparisons. Third, individual judges again exhibited a wide range of sensitivity as well as of tolerance. Fourth, there was some further indication of greater diversity in individual assessments of moderately unpalatable samples.

The significant degree of correlation of the panel assessments with the sodium chloride and nitrate content of the test material is a satisfactory

feature of the present findings. From the regression equation given in the preceding section it may be computed that the degree of saltiness to the taste preferred by this panel would be obtained from a sodium chloride content of about $4\frac{3}{4}\%$ by weight of the cooked bacon in the absence of sodium nitrate, and of roughly 4% when $2\frac{1}{2}$ parts per thousand of sodium nitrate was also present.

Acknowledgments

The data reported upon were recorded in the course of studies by Dr. N. E. Gibbons and Mr. G. A. Grant of the Food Investigations Group of these laboratories. Mr. F. L. Smith assisted largely in the statistical computations.

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FLAVOUR REVERSION IN HYDROGENATED LINSEED OIL

III. THE RELATION OF ISO-LINOLEIC ACID TO FLAVOUR DETERIORATION[1]

By H. W. Lemon[2]

Abstract

Further evidence that iso-linoleic acid is related to the unpleasant odour development when partially hydrogenated linseed oil is heated is as follows:

(*a*) Partially hydrogenated perilla oil, containing considerable iso-linoleic acid, developed the same odour when heated, as did partially hydrogenated linseed oil.

(*b*) A concentrate of iso-linoleic acid developed a similar odour when it was heated. Distillation of the acid, or removal of unsaponifiable substances, had no effect on the odour development.

(*c*) When fatty acid fractions obtained by crystallization of the acids from hydrogenated linseed oil were re-esterified with glycerol, and subjected to the heat test, most odour development occurred in the fraction containing most iso-linoleic acid.

Increasing the selectivity of hydrogenation did not greatly affect the formation or hydrogenation of iso-linoleic acid. However, products of high temperature (200° to 250° C.) hydrogenations were softer for equivalent iodine numbers, and had lower melting points than those from low temperature hydrogenations.

Hydrogenation of partly polymerized linseed oil yielded a product that when heated did not develop the characteristic odour of hydrogenated linseed oil.

It was reported in a previous publication (8) that when linseed oil is hydrogenated an isomeric linoleic acid is formed in which the double bonds are in such positions that they will not form a conjugated system upon alkali isomerization. Some experimental evidence was presented that indicated that the isomeric acid may be responsible for the characteristic odour that develops when partially hydrogenated linseed oil is heated to baking and frying temperatures. It was suggested that hydrogenation of linseed oil should be highly selective in order that the iso-linoleic acid may be completely hydrogenated without the formation of large quantities of saturated acids.

In the present paper further evidence that iso-linoleic acid plays a part in flavour development on heating is presented, together with the results of experiments to reduce its amount in the product: (*a*) by increasing the selectivity of hydrogenation and (*b*) by reducing the linolenic acid content of linseed oil by polymerization.

Methods

Analytical methods and the techniques used for refining, bleaching, hydrogenation, and deodorizing have been described (8). Linolenic and linoleic acids were determined by the spectral method of Mitchell, Kraybill, and

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[2] *Research Fellow.*

Zscheile (10) as modified by Brice, Swain, Schaeffer, and Ault (6). Saturated and iso-oleic acids were determined by the method of Baughman and Jamieson (4).

Polymerization of linseed oil was done in a 2 litre three-necked flask equipped with thermometer, a tube for bubbling carbon dioxide through the oil, and a goose neck leading to a condenser. The reaction was carried on under vacuum at 315° C.

Experimental and Results

A. Relation of Iso-linoleic Acid to Odour Development

Hydrogenation of Perilla and Tung Oils

The amount of linolenic acid in perilla oil is as much as, or more than, that in linseed oil, and so perilla oil might be expected to yield a hydrogenation product similar in respect to flavour reversion characteristics to that produced by linseed oil. Tung oil contains a large proportion of eleostearic acid, an isomer of linolenic acid, and it is unlikely that its hydrogenation would produce the same iso-linoleic acid as hydrogenation of linolenic acid. Therefore, a quantity of each of these oils was hydrogenated to a plastic consistency, and samples subjected to the heat test.

The perilla oil was alkali-refined, hydrogenated, and deodorized in the usual manner. Samples were taken for fatty acid analysis, and the results are given in Fig. 1. As in the case of linseed oil, iso-linoleic acid was produced

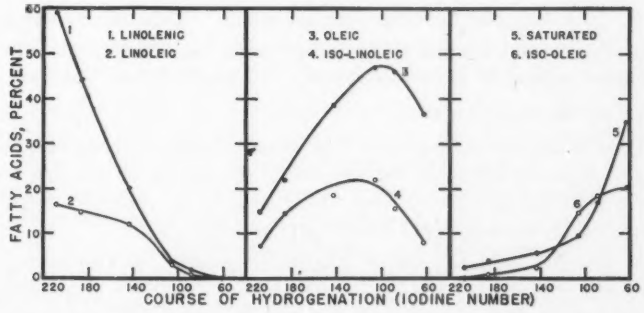

FIG. 1. *Progressive change in fatty acid composition on hydrogenation of perilla oil.*

on hydrogenation. The tung oil was hydrogenated without refining. Samples were examined for diene and triene conjugation before and after alkali isomerization with the use of a Beckman spectrophotometer; the absorption curves are shown in Fig. 2. Saturated and iso-oleic acids were not determined. There was a decrease in triene conjugation on hydrogenation but very little development of diene conjugation. Alkali isomerization had little effect on the amount of diene and triene conjugation present. These results indicate that, when eleostearic acid is hydrogenated under the conditions described, two or more double bonds are saturated simultaneously.

The hydrogenated perilla, linseed, and tung oils, and a standard all-hydrogenated shortening were heated to 200° C. The hydrogenated perilla and hydrogenated linseed oils developed the same unpleasant odour, the two being indistinguishable. The hydrogenated tung oil, with an apparent iodine

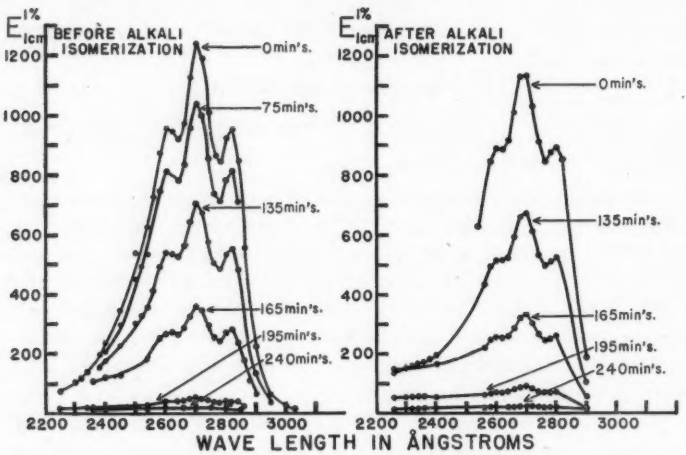

FIG. 2. *Effect of hydrogenation time on ultraviolet absorption by tung oil.*

number of 58.6, did not develop such an odour. This experiment provided further evidence that the substance responsible for the unpleasant odour of hydrogenated linseed oil is formed by the hydrogenation of linolenic acid.

Heat Tests on Iso-linoleic Acid

It was stated in the first paper of this series (8) that a strong odour resembling that of heated hydrogenated linseed oil developed on heating a distilled iso-linoleic acid concentrate. The odour was quite different from that of linolenic, linoleic, or oleic acids treated in the same way.

It was thought that the odour might be caused by some unsaponifiable substance associated with the iso-linoleic acid. Therefore a quantity of the acid in alcoholic solution was neutralized with potassium hydroxide, diluted with water, and the soap solution extracted several times with ether. The acids were liberated from the soap, washed with water, dried, and distilled from a Hickman alembic flask. On heating, the acids developed the same strong odour, resembling that of hydrogenated linseed oil.

Fractional Crystallization of Fatty Acids from Hydrogenated Linseed Oil

The isolation of a concentrate of iso-linoleic acid by low temperature crystallization of the separated fatty acids of hydrogenated linseed oil was described in the first paper of this series (8). In a similar separation, four fatty acid fractions were obtained. The first of these consisted of the acids that precipitated from acetone at −30° C.; the second fraction precipitated

at from −30° to −60° C. The third fraction consisted of all of the crystalline precipitates that could be obtained by chilling to −60° C. the concentrated filtrate from the previous precipitations, and the fourth fraction, consisting largely of iso-linoleic acid, was obtained from the final filtrate.

Each of these fractions was esterified with glycerol in the proper amount to yield triglyceride. The products were deodorized. The fat made from the first fraction was quite hard, that from the second fraction was semisolid, and those from the third and fourth fractions were liquid at room temperature.

The four fats were heated to 200° C. There was little, if any, development of the reverted odour in the first fat but the fourth fat developed a very strong odour. Numbers two and three were similar, and intermediate to numbers one and four. There was no doubt that the odour development was caused by heating the iso-linoleic glyceride itself, or some substance associated with it.

B. Influence of Selectivity on Hydrogenation of Iso-linoleic Acid

It was felt that hydrogenated linseed oil would be more suitable for use as a shortening if the iso-linoleic acid content were reduced or eliminated, and it was thought that some improvement might be made by increasing the selectivity of hydrogenation. It has been pointed out by Bailey, Feuge, and Smith (2) that selectivity is increased by raising the temperature or catalyst concentration, and by decreasing the pressure or agitation, and that each of the conditions contributing to selectivity causes a greater formation of iso-oleic acid.

Three series of hydrogenations were completed. In the first series the temperature was kept low during the initial period of the hydrogenations but was raised rapidly when the refractive index (Zeiss butyro) had dropped to about 58 at 40° C. corresponding to an iodine number of approximately 120; at the same time the gauge pressure was reduced from 25 to 5 lb. It was hoped that increasing the temperature at about iodine number 120 would suppress the rapid formation of saturated acids which normally begins at about this point, and at the same time favour the hydrogenation of iso-linoleic acid. Various temperature combinations were tried. In the second and third series of hydrogenations, four temperatures between 120° and 250° C. were selected, and the oil and catalyst mixtures were brought to these temperatures as rapidly as possible. A slight positive pressure of hydrogen was maintained during the period required to bring the oil to the desired temperature; it was then increased to 25 lb. gauge pressure.

In all three series, samples were taken at intervals during the hydrogenations for fatty acid analysis. The results are given in Table I. By plotting these results against iodine number, saturated and iso-linoleic acid values at iodine number 90 were determined for the low to high temperature series. These values are given in Table II. It is apparent that raising the temperature of hydrogenation at iodine number 120 had no appreciable effect on the subsequent hydrogenation of iso-linoleic acid.

TABLE I

ANALYSIS OF HYDROGENATED LINSEED OIL SAMPLES

Hydrogenation temperature, °C.	Time, min.	Iodine number	Fatty acid composition, %					
			Saturated	Iso-oleic	Oleic	Iso-linoleic	Linoleic	Linolenic
Series I. Low to high temperature hydrogenations								
140	20	148.5	7.4	1.9	40.8	5.6	15.2	29.1
140	40	120.8	10.1	4.0	48.1	14.9	10.9	12.0
140	60	94.4	17.0	7.5	50.9	17.1	5.4	2.1
140	70	79.6	23.1	10.7	50.1	13.8	1.8	0.5
115-190	30	163.2	6.5	0.9	36.0	1.5	17.0	38.1
115-190	75	119.6	10.9	3.4	46.9	16.8	11.5	10.5
115-190	100	97.8	13.6	9.0	51.7	20.5	3.9	1.3
115-190	115	79.2	21.5	19.0	45.9	13.5	0.1	0
115-240	45	147.0	7.4	1.5	40.1	8.2	16.6	26.2
115-240	80	112.4	11.9	3.9	48.6	18.7	10.2	6.7
115-240	95	89.0	15.0	15.4	51.4	16.6	1.2	0.4
115-240	100	82.8	17.1	22.8	46.6	13.4	0.1	0
140-190	20	152.3	8.2	2.3	36.3	5.1	17.1	31.0
140-190	50	108.1	12.2	6.9	48.3	19.4	8.2	5.0
140-190	60	96.4	14.3	12.1	49.0	18.9	4.1	1.6
140-190	75	81.9	17.7	16.7	52.7	12.7	0.2	0
140-235	25	146.0	7.9	2.1	39.6	7.8	16.4	26.2
140-235	45	106.7	12.1	5.5	51.6	17.4	8.2	5.2
140-235	55	84.3	18.2	16.4	50.3	12.9	1.2	1.0
140-235	60	72.0	23.0	28.8	41.0	6.4	0.5	0
Series II. Effect of temperature of hydrogenation on selectivity								
120	60	132.5	10.0	2.8	40.3	18.3	12.4	16.2
120	90	106.4	14.6	6.0	46.4	20.4	7.7	4.9
120	120	88.1	20.9	8.3	49.0	16.6	3.8	1.4
120	155	70.5	31.2	10.0	46.0	11.6	1.0	0
150	30	128.0	10.3	3.3	42.1	18.2	12.2	13.9
150	45	103.7	15.2	6.3	47.3	20.4	6.5	4.3
150	60	80.3	25.3	9.7	48.8	15.2	1.0	0.8
150	80	53.9	43.7	10.8	39.2	6.1	0.2	0
200	25	93.5	14.6	14.3	49.3	18.1	2.3	1.4
200	30	80.1	20.4	15.9	50.7	12.0	0.6	0.4
200	40	59.9	36.4	17.9	39.7	5.7	0.3	0
200	45	47.8	47.7	14.3	34.7	3.2	0.1	0
250	20	95.6	12.0	17.6	48.7	17.5	2.9	1.3
250	25	80.9	18.8	23.4	45.0	12.2	0.6	0
250	30	67.5	26.8	27.6	40.3	5.1	0.2	0
250	35	56.8	37.6	20.4	38.3	3.6	0.1	0

TABLE I—*Continued*

ANALYSIS OF HYDROGENATED LINSEED OIL SAMPLES—*Continued*

Hydrogenation temperature, ° C.	Time, min.	Iodine number	Fatty acid composition, %					
			Saturated	Iso-oleic	Oleic	Iso-linoleic	Linoleic	Linolenic
Series III. Effect of temperature of hydrogenation on selectivity								
120	60	146.0	9.7	2.5	32.6	18.1	13.8	23.3
120	120	105.6	16.4	8.5	40.2	21.4	6.5	6.0
120	160	80.4	27.2	11.3	42.0	16.1	2.3	1.1
120	170	72.8	30.9	10.3	44.0	12.9	1.1	0.8
120	190	58.7	39.7	9.5	42.7	7.5	0.6	0
150	25	135.4	9.3	4.3	38.9	17.0	12.2	18.3
150	50	103.7	12.6	12.2	46.6	18.9	5.4	4.3
150	65	83.9	19.7	17.0	46.0	16.2	1.1	0
150	75	75.0	25.7	17.3	42.1	13.4	0.5	0
150	95	49.8	45.9	16.5	33.6	4.0	0	0
200	25	116.6	8.6	12.0	45.4	15.4	9.0	9.6
200	33	93.8	10.9	26.0	43.7	18.1	0.8	0.5
200	42	82.2	16.5	32.9	39.5	11.1	0	0
200	51	67.8	27.1	30.7	36.2	6.0	0	0
200	55	62.0	31.8	27.9	36.1	4.2	0	0
240	20	115.8	9.6	11.8	43.2	18.7	8.4	8.3
240	24	103.1	10.3	18.4	43.6	21.1	4.4	2.2
240	33	90.7	13.6	22.6	44.8	17.8	1.2	0
240	45	78.0	19.3	23.4	47.4	9.5	0.35	0
240	65	65.7	27.8	23.6	43.3	5.3	0	0

TABLE II

EFFECT OF RAISING THE TEMPERATURE DURING HYDROGENATION ON THE CONTENT OF SATURATED AND ISO-LINOLEIC ACIDS AT IODINE NUMBER 90

Hydrogenation temperature, ° C.	Saturated acids, %	Iso-linoleic acid, %
140	19.0	16.5
115-190	16.5	18.5
115-240	15.0	16.5
140-190	15.5	17.5
140-235	16.0	15.0

In Fig. 3 the effect of temperature of hydrogenation on fatty acid composition at iodine numbers 80 and 90 is shown for Series II hydrogenations. Increasing the temperature caused more complete hydrogenation of linolenic and linoleic acids, increased formation of iso-oleic acid, and decreased produc-

tion of saturated acids; however, it had little effect on the hydrogenation of iso-linoleic and oleic acids. These conclusions are in agreement with those of Bailey and Fisher (3), who found that iso-linoleic acid is much more resistant to hydrogenation than linoleic or linolenic acids.

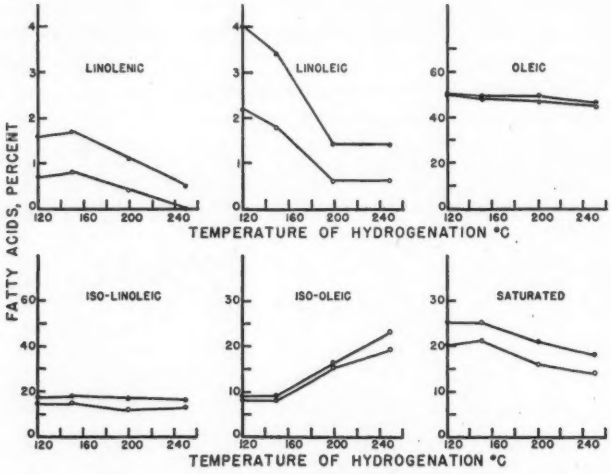

FIG. 3. *Effect of temperature of hydrogenation on the fatty acid composition of hydrogenated linseed oil.*

The melting points of samples from Series III hydrogenations were determined by the capillary tube method, and their micropenetration values at 25° C. were determined with a micropenetrometer similar to that described by Feuge and Bailey (7). The values obtained have been plotted against iodine numbers (Fig. 4). It is evident that the melting points of samples taken from the high temperature hydrogenations were lower for equivalent iodine numbers than those of samples taken from the low temperature hydrogenations. Similarly, the penetration values at 25° C. of samples from the high temperature hydrogenations were greater than those of samples of the low temperature hydrogenations for equivalent iodine numbers, although the difference became less as hydrogenation proceeded.

From the results, the iodine number corresponding to a melting point of 47° C. has been estimated for hydrogenations done at 250°, 200°, 150°, and 120° C., respectively, and the fatty acid composition for each of these iodine numbers has been determined from the results in Table I. These values are given in Table III.

It can be concluded that if linseed oil is hydrogenated at a high temperature, it can be saturated to a lower iodine number without becoming too hard, giving a product with a lower iso-linoleic acid content. However, when samples having a lower iso-linoleic acid content were heated, there was still a

strong odour development, and it was difficult to determine whether there was any improvement.

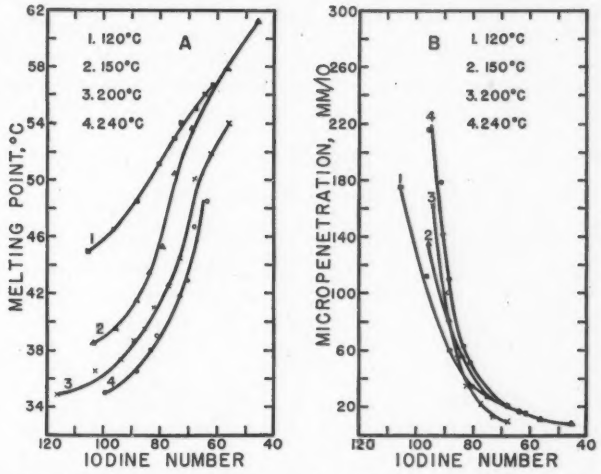

FIG. 4. *Effect of temperature of hydrogenation of linseed oil on melting point (Graph A) and on micropenetration at 25° C. (Graph B).*

TABLE III

EFFECT OF TEMPERATURE OF HYDROGENATION OF LINSEED OIL ON THE FATTY ACID COMPOSITION AT MELTING POINT OF 47° C.

Hydrogenation temperature, °C.	Iodine number	Fatty acid composition, %					
		Saturated	Iso-oleic	Oleic	Iso-linoleic	Linoleic	Linolenic
120	94	21.2	10.3	41.7	19.2	4.4	3.3
150	79	22.5	17.2	44.5	14.5	0.7	0
200	70	25.0	31.4	37.0	6.5	0	0
240	66	27.5	23.6	43.5	5.5	0	0

C. HYDROGENATION OF POLYMERIZED LINSEED OIL

When linseed oil is polymerized, there is a reduction in the linolenic and linoleic acids content. There is a commercial process in operation that entails polymerization followed by extraction of the non-polymerized portion with acetone (5). As this results in an oil with a low concentration of linolenic acid it has been suggested that the oil might be used as an edible oil. Privett, Pringle, and McFarlane (11) have developed a similar process, involving milder polymerization, for the purpose of obtaining an edible fraction from linseed oil. In view of this work it was decided to determine quantitatively by the spectral method the disappearance of linolenic and linoleic acids on

polymerization, and to hydrogenate oils polymerized to varying degrees and apply heating tests in order to determine their susceptibility to reversion.

Polymerization was carried on for 20 min., one hour, two hours, and three hours. Refractive index, free fatty acid, and linolenic and linoleic acids were determined for each product. The results are given in Table IV. It is evident that, although the disappearance of linolenic acid on polymerization is rapid, there is still some present after heating for three hours.

TABLE IV

POLYMERIZATION OF LINSEED OIL

Time of polymerization	Refractive index, 50° C.	Free fatty acid, % as oleic	Linoleic acid, %	Linolenic acid, %
0 min	1.4699	0.05	19.6	51.9
20 min.	1.4715	1.2	14.4	43.1
1 hr.	1.4744	1.8	13.9	26.6
2 hr.	1.4771	2.8	11.2	13.9
3 hr.	1.4790	3.7	9.1	7.5

Each of the polymerized oils was hydrogenated without any further treatment. The hydrogenations proceeded with some difficulty, probably owing to the high free fatty acid content. The products were deodorized, and samples heated to 200° C. on a hot plate. The hydrogenated linseed odour was present in the product from the 20 min. polymerization, but there was little, if any, of it in the others.

Discussion

There is considerable evidence that the unpleasant flavour and odour of heated hydrogenated linseed oil are caused by the decomposition of iso-linoleic acid, although there is some indication from storage tests (9) that this is not the only cause of flavour deterioration. Reversion in unhydrogenated oils, such as soybean, is not explained by the iso-linoleic acid theory, and it is probable, as has been suggested by Bailey (1), that in this case it is the result of a different mechanism.

If iso-linoleic acid plays a part in reversion its removal from hydrogenated linseed oil presents a difficult problem. The results of the experiments to determine the effect of selectivity on its hydrogenation were not encouraging, as it apparently hydrogenates with difficulty, and quantities of it persist until the product has become very hard regardless of the conditions of hydrogenation.

Acknowledgments

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FLAVOUR REVERSION IN HYDROGENATED LINSEED OIL

IV. FURTHER PROCESSING STUDIES[1]

By H. J. Lips[2]*, H. W. Lemon[3], and G. A. Grant[4]

Abstract

Flavour reversion could not be detected in samples of hydrogenated linseed oil stored under vacuum in the dark. In samples exposed to the air, reversion occurred without appreciable increase in peroxide oxygen or Kreis values, particularly in products of low iodine number, while accompanying changes in fluorescence were slight and erratic. An observed 'bad area' for susceptibility in the lower iodine number range suggests that iso-linoleic acid (4) is not the only cause of reversion. No improvement in flavour stability was obtained by: low to high temperature hydrogenation (110° to 240° C. (230° to 464° F.)), removal of impurities from the oil, or the use of a linseed oil fraction from a commercial polymerization process.

A previous paper in this series (6) dealt with storage studies to determine the effect of various modifications in processing procedure upon the susceptibility of hydrogenated linseed oil to flavour reversion. The present investigation is an extension of that work.

Experimental

Standard processing techniques, the method of estimating storage life by flavour scores, and some of the chemical measurements used have been described (4, 6). In this study some of the samples were stored at 60° C., rather than at 43.3° C., to obtain comparative results in a shorter time. As earlier work demonstrated that any chemical changes accompanying flavour reversion would be difficult to detect, sensitive modifications of the peroxide oxygen (7) and Kreis (12, 13) tests were introduced as estimates of oxidative deterioration. To investigate possible changes in fluorescence, readings of xylol solutions of the fat were made in a Coleman photofluorometer (3).

Vacuum Storage

It has not been clearly established that the presence of oxygen is essential for flavour reversion (10). To examine the effects of oxygen-free storage on hydrogenated linseed oil, melted samples were evacuated in glass tubes on a high vacuum apparatus for four hours, and sealed off at a pressure of 5μ. These tubes were stored in the dark at 43.3° C. together with an untreated control sample of the same shortening.

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* *Earlier publications by this author appeared under the name A. Lips.*

The control sample developed definite flavour reversion in 11 weeks while the vacuum-stored material had no detectable reverted odour at the end of 60 weeks' storage. The control had a peroxide value of 2.4 ml. of 0.002 *N* thiosulphate per gm. (iodimetric method) at the end of 11 weeks. At 60 weeks the peroxide value of the vacuum-stored material was nil, even by the more sensitive ferrometric procedure.

Removal of Impurities

A number of attempts have been made to account for flavour reversion on the basis of impurities in oils. Voskresenkii and Dobruinina (11), working on soybean oil, reported an odorous constituent that had a variable nitrogen content and reduced Fehling's solution. Marcelet (8) isolated from vegetable oils saturated and unsaturated hydrocarbons having nauseous odours, and Bickford (2) isolated similarly objectionable material from the condensate obtained from a commercial soybean oil deodorizer.

Removal of possible sources of flavour instability in linseed shortening was attempted by deodorizing and by winterizing refined and bleached linseed oil, before hydrogenating and deodorizing in the usual manner. Table I shows the negative results. Preliminary deodorization at 270° C. was strongly detrimental, as evidenced by a short storage life and a high mean peroxide value.

Low to High Temperature Hydrogenation

Previous investigations on the effect of different conditions of hydrogenation upon flavour stability were continued. A selective hardening of linseed oil is desirable because of the high proportion of linolenic acid that must be hydrogenated. It is also important that the formation of iso-linoleic acid be minimized, since the breakdown of this compound is considered to be a cause of flavour reversion (4).

A hydrogenation procedure in which the temperature was raised during the process from a low to a high value appeared to offer a means of hydrogenating iso-linoleic acid without building up a high concentration of saturated acids (5). A series of samples of linseed shortening was prepared in the manner previously described, employing temperatures in the range 110° to 240° C., and available commercial- and laboratory-prepared nickel catalysts (4, 6). Temperature ranges, catalysts, peroxide values (iodimetric method) averaged over the entire sampling period (56 weeks), and storage lives are given in Table I. Storage tests at 43.3° C. showed no improvement in the products obtained over the average for standard processing. Mean peroxide values were low, except in the case of one of the 110° to 160° C. samples, indicating the usual resistance to oxidation.

Hydrogenation to Various Iodine Numbers

Earlier work reported susceptibility to flavour reversion at a maximum at iodine value 80 to 130, with complete stability at iodine value 6 (4, 6). It was assumed that susceptibility varied with the amount of iso-linoleic acid present.

TABLE I

STORAGE LIFE AND MEAN PEROXIDE VALUE OF LINSEED SHORTENINGS PREPARED BY VARIOUS PROCESSING PROCEDURES AND STORED AT 43.3° C. FOR 56 WEEKS

Group	Group variant			Storage life, weeks	Mean peroxide value*, ml. per gm.
	Alkali treatment, ° Bé	Catalyst	Temperature range, ° C.		
Low to high temperature hydrogenation	30	Standard	110–160	18	8.1
	30	Standard	110–160	29	3.7
	30	Standard	110–190	17	1.0
	30	Standard	110–190	17	3.5
	30	Standard	115–190	17	3.1
	30	Standard	115–240	19	1.0
	30	Standard	140–190	15	1.3
	30	Standard	140–235	16	0.8
	30	Commercial	110–160	25	2.5
	30	Commercial	110–190	31	1.6
	30	Commercial	110–160	17	4.4
	30	Commercial	110–190	32	2.0
	40	Standard	115–190	15	1.2
	40	Standard	115–190	6	1.3
Additional deodorization	Deodorized at 200° C. before hydrogenation			16	9.6
	Deodorized at 270° C. before hydrogenation			1	31.6
Use of winterized oil	Winterized at 0° C. after refining			18	2.6
Average for 18 samples by standard procedure				29	
Estimated necessary difference				12	

* *Iodimetric method (13).*

However, it has since been noticed that flavour reversion is often pronounced at iodine values considerably lower than those that would be expected from the theory that iso-linoleic acid is the cause of reversion. This phenomenon was investigated further.

Two hydrogenations were carried out according to the usual processing technique in a large converter, so equipped as to permit removal of samples of varying degrees of saturation while the operation continued. Samples thus obtained were deodorized, stored at 60° C., and sampled at weekly intervals for nine weeks. Composition data for the two series are shown in Table II, and storage lives and mean values for peroxide oxygen (ferrometric method), Kreis test, and fluorescence are presented in Table III (*A*).

It will be seen that for both series of hydrogenated oils there was no regular improvement in storage life with decreasing iso-linoleic acid concentration. There was in fact an apparent slump in flavour stability at lower iodine values, contrary to previous observations based on a rapid heat test (6). It will also be noted that storage lives in the two series were not the same for similar

TABLE II

COMPOSITION OF SAMPLES OF HYDROGENATED LINSEED OIL OF DIFFERENT IODINE NUMBERS

Time of hydrogenation, min.	Iodine number	Fat acid content*, %					
		Saturated	Iso-oleic	Oleic	Iso-linoleic	Linoleic	Linolenic
Series 1							
33	88.3	20.9	10.4	47.6	15.4	3.5	2.2
38	77.3	27.1	12.9	44.2	13.0	1.8	1.0
45	60.8	38.7	13.1	38.9	8.5	0.8	0
49	52.8	44.3	12.2	37.8	5.3	0.4	0
53	40.2	55.6	8.2	33.8	2.0	0.4	0
58	39.9	—	—	—	—	0.3	0
Series 2							
35	89.4	20.6	10.3	49.0	15.1	3.8	2.2
42	77.6	26.7	11.3	45.8	13.7	1.8	0.7
50	62.2	37.4	12.7	40.0	9.2	0.7	0
54	53.6	44.0	12.1	37.6	5.9	0.4	0
58	48.2	47.4	8.8	40.3	3.2	0.3	0
62	42.2	53.2	8.0	36.4	2.0	0.3	0

**For method of determination see Ref. (4).*

TABLE III

MEAN PEROXIDE, KREIS AND FLUORESCENCE VALUES, AND STORAGE LIVES, FOR LINSEED SHORTENINGS STORED AT 60° C. FOR NINE WEEKS

Group	Group variant	Mean values of measurements on stored samples			Storage life[3], weeks
		Peroxide oxygen content*, m.e. per kgm.	Kreis value, extinction coefficients	Fluorescence, photo-fluorometer units	
A. Varying iodine number	Series 1				
	88.3	53.9	44.2	72.0	2.4
	77.3	22.8	22.0	74.0	2.2
	60.8	9.7	9.0	64.5	3.6
	52.8	9.7	8.3	60.7	2.8
	40.2	6.7	5.7	61.7	3.2
	39.9	4.5	5.9	58.4	4+
	Series 2				
	89.4	42.2	36.1	70.3	1.8
	77.6	24.3	20.5	68.6	1.8
	62.2	9.2	9.2	63.6	3.9
	53.6	8.3	7.2	60.2	3.6
	48.2	6.8	6.3	56.7	3.0
	42.2	5.9	4.8	56.2	5+
B. Commercial polymerized oil fraction	Hydrogenated	14.9	22.4	48.9[1]	0.7
	Hydrogenated	30.9	27.5	39.8[1]	0.5
	Esterified and hydrogenated	70.5	23.4	56.5[2]	1.8

** Ferrometric method (7).*
[1] 1 : 50 dilution.
[2] 1 : 100 dilution. All other fluorescence measurements 1 : 10 dilution.
[3] Estimated necessary difference: one week.

iodine values. This may have been due to different rates of hydrogenation, since the composition data do not indicate any reason for the discrepancies.

At the higher iodine values there was some increase in Kreis and peroxide values before the appearance of definite flavour reversion. This increase was steady with no definite changes in the rate of accumulation and appeared to be independent of reversion. Below iodine number 60 these values remained practically stationary. Fluorescence showed a decrease during storage but the changes were erratic throughout. Fluorescence values were generally higher at the higher iodine numbers.

Use of Polymerized Oils

In view of the stability to reversion found in hydrogenated, acetone-segregated fractions of polymerized linseed oil (9), a commercial product (1) obtained by solvent extraction of polymerized linseed oil was examined. In addition to the regular polymerized fraction, two laboratory-prepared materials (5) were hydrogenated.

The commercial process of acetone extraction of polymerized linseed oil yields an oil that is very dark in colour, and has a 'strong bodied oil' odour. The free fatty acid content is high, about 13% expressed as oleic acid, and this cannot be removed by ordinary refining methods, since emulsifying properties prevent the 'break'. Alkali refining has been found unsuccessful even after lengthy steam deodorization, so the regular commercial fraction was esterified with glycerol to reduce the free fatty acid content to 1.6%. Refractive index, linoleic acid, linolenic acid, and free acid content for all three samples are shown in Table IV. The linoleic and linolenic acid contents

TABLE IV

ANALYSIS OF SOLVENT SEGREGATED FRACTIONS OF POLYMERIZED LINSEED OIL

Sample	Refractive index at 50° C.	Linoleic acid, %	Linolenic acid, %	Free fatty acid as oleic, %
Laboratory sample	1.4736	14.4	33.0	2.1
Laboratory sample	1.4729	11.5	22.3	3.6
Regular process sample, esterified with glycerol	1.4750	9.3	8.3	1.6

of the laboratory-prepared fractions were high since these were obtained from only partially polymerized oils. However, even in the regular product the content of these acids was still appreciable.

The three samples were hydrogenated with difficulty (5). There was considerable foaming of the oils, and on deodorizing a large amount of crystalline material (acid number 126.5) tended to choke the side-arm of the deodorizing flask. The final products were dark coloured. Owing to the

presence of polymerized acids in the products, saturated acids could not be estimated by the usual method and hence the amount of iso-linoleic acid could not be determined.

The products were stored at 60° C. as outlined in the preceding section. Storage lives and mean values for the chemical tests are shown in Table III (*B*). Storage lives were short, although there was some doubt among members of the testing panel that the off-odours developed were typical reverted odours of hydrogenated linseed oil. As indicated by the high mean values for peroxide and Kreis tests these products were unstable to oxidation. Mean fluorescence was much higher than with ordinary linseed shortening.

Discussion

The experiments outlined indicate no solution to the flavour reversion problem by removal of impurities from the oil, by selective hydrogenation, or by the use of solvent-segregated material from a commercial polymerization process.

The failure of selective hydrogenation to minimize reversion may be explained in part by the finding that iso-linoleic acid is more resistant to hydrogenation than linoleic or linolenic acids (5). The use of commercial fractions of polymerized oils does not appear promising, because of their high colour and free fatty acid, and emulsifying properties. Moreover, the polymerization does not alter all the linolenic acid, and the hydrogenated products are unstable to oxidation and contain polymerized material of undetermined nature. However, it must be emphasized that the commercial process is not identical with the procedure reported by Privett, Pringle, and McFarlane (9), which yields a more acceptable product.

The storage experiments with shortenings of various iodine values suggest that iso-linoleic acid is not the only cause of reversion. They also confirm earlier views that flavour changes may occur without appreciable oxidative changes, although the vacuum storage results are evidence that some oxygen must be present for reversion to take place.

Acknowledgments

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RATION BISCUITS

IV. EFFECT OF TEMPERATURE AND SHORTENING TYPE ON KEEPING QUALITY[1]

By H. J. Lips[2]*, N. C. Crowson[3], and W. Harold White[4]

Abstract

Biscuits commercially prepared with shortenings of four types (compound animal–vegetable, blended vegetable, hydrogenated vegetable, and stabilized, hydrogenated vegetable) were coarsely ground and stored in sealed cans at 26.7°, 43.3°, and 60° C. (80°, 110°, and 140° F.). Deterioration was assessed by peroxide oxygen and pH determinations, and by flavour scores. The results obtained for biscuits stored at 60° C. were not indicative of behaviour at the lower temperatures. Flavour score was the most useful estimate of biscuit keeping quality, especially at 26.7° and 43.3° C. Peroxide development was appreciable only in biscuit material stored at 26.7° C.

Biscuits prepared with hydrogenated vegetable shortenings were generally more stable (average storage life: 84, 22, and 13 weeks at 26.7°, 43.3°, and 60° C., respectively) than those prepared with animal–vegetable or blended vegetable shortenings. However, shortenings with Swift stabilities (110° C.) greater than 40 hr. did not yield products of increased keeping quality.

Introduction

One of the important causes of spoilage in baked goods is deterioration of the fat used in their preparation. Therefore it might be expected that the keeping quality of a baked product would bear a direct relation to the keeping quality of the shortening used. However, determination of shortening stability does not necessarily indicate the stability that the shortening will show in soda crackers (4, 12, 13). This has been attributed in part to destruction of antioxidants and peroxides in the fat during baking.

A previous investigation in these laboratories demonstrated that ration biscuits had a longer storage life at 43.3° C. when a stabilized, hydrogenated vegetable, rather than a compound, animal–vegetable shortening was used (5). The present paper describes an examination of a number of biscuit shortenings and the results obtained from storage tests on ration biscuits prepared with these shortenings.

Materials and Methods

Seventeen currently available shortenings (1943) were classified according to information received from the manufacturers into four general groups: I,

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* *Earlier publications by this author appeared under the name A. Lips.*

compound animal–vegetable; II, blended all vegetable; III, hydrogenated vegetable; and IV, stabilized, hydrogenated vegetable. Keeping quality was estimated by Swift stability tests at 110° C. (9) and by peroxide measurements (15) at 10 appropriate intervals on samples stored in loosely covered half-pint jars for 38 weeks at 26.7° C. Capillary melting point (15), Kaufman iodine number (15), refractive index at 48° C. (15), saponification number (1), and smoke point (1) were determined on the fresh material.

The experimental biscuits were prepared by two commercial manufacturers. Processing was carried out according to the formula: 50 lb. of soft wheat flour, 5 lb. of shortening, baking soda (6 oz., Plant *A*; 8 oz., Plant *B*), and water as used in plant practice. Shortenings (described above) and flour used by both manufacturers were obtained from the same sources. The amount of moisture in the biscuits produced was quite uniform, but the fat content was generally higher for Plant *A* products (Table I).

TABLE I

MEAN MOISTURE AND FAT CONTENTS OF BISCUITS PREPARED WITH FOUR TYPES OF SHORTENING IN TWO PLANTS

Biscuit group	No. of samples in group		Fat and moisture contents, %			
			Plant *A*		Plant *B*	
	Plant *A*	Plant *B*	Fat	Moisture	Fat	Moisture
I. Compound animal–vegetable shortenings	4	3	10.4	7.5	7.8	7.1
II. Blended vegetable shortenings	2	2	10.7	6.6	8.4	6.5
III. Hydrogenated vegetable shortenings	6	3	10.2	7.3	8.0	6.6
IV. Stabilized, hydrogenated vegetable shortenings	5	4	10.3	7.3	8.0	6.8

Each lot of biscuits was sampled and ground. Portions of the material (120 gm.) were placed in laminated glassine bags, and each bag was sealed in a No. 1 tin can. This left about one inch of headspace.

Biscuits prepared by Plant *A* with 12 of the 17 shortenings were stored at 26.7°, 43.3°, and 60° C., while those prepared with the five remaining shortenings were stored at 60° C. Biscuits made with the same 12 shortenings at Plant *B* were stored only at 60° C. The plant products were compared at 60° C. because this is the usual temperature employed in the Schaal incubation test for fats and fat-containing materials (6, p. 125). Flavour score of the biscuit, peroxide oxygen value of the extracted fat, and pH of a potassium chloride extract of the biscuit material were determined at each sampling (5).

Samples were taken at 15 suitable intervals during total storage periods of 82, 48, and 30 weeks at temperatures of 26.7°, 43.3°, and 60° C., respectively.

Shortening and biscuit data were examined statistically by means of analyses of variance and by calculation of simple coefficients of correlation.

Results

Shortenings

Group mean values for measured properties are shown in Table II, and peroxide development is further illustrated in Fig. 1.

TABLE II

MEAN VALUES FOR MEASURED PROPERTIES OF 17 BISCUIT SHORTENINGS OF FOUR TYPES

Shortening group	No. of samples in group	Measurements						
		Melting point, ° C.	Iodine No.	Refractive index (at 48° C.)	Saponification No.	Smoke point, ° F.	Swift stability, hr. at 110° C.	Mean peroxide value, ml. of 0.002 *N* thiosulphate per gm. (over all samplings for 38 weeks' storage at 26.7° C.)
I. Compound animal–vegetable	4	45.1	70.5	1.4589	192.7	420	9	126.8
II. Blended vegetable	2	42.5	77.9	1.4591	192.2	426	13	22.9
III. Hydrogenated vegetable	6	43.8	68.1	1.4579	189.9	425	20	11.4†
IV. Stabilized, hydrogenated vegetable	5	43.6	59.0	1.4568	190.8	424	66	0.8‡
Smallest necessary difference between any two groups for statistical significance (5% level)		—	8.9	0.0012	—	—	12	30.9

† *Three shortenings only.*
‡ *Four shortenings only.*

Statistical calculation showed no significant differences in mean value between shortening groups for melting point, saponification number, and smoke point; significant differences for iodine number and refractive index; and highly significant differences for Swift stability and mean peroxide value. Group IV shortenings were lower in iodine value than those of Groups I, II, and III and lower in refractive index than those of Groups I and II. Swift stability was higher for Group IV than for the other three groups and mean peroxide value was higher for Group I than for the other three.

Iodine number, refractive index, Swift stability, and log mean peroxide value were interrelated (Table III). Low iodine number was associated with low refractive index and high stability. Saponification number was inversely related to smoke point.

TABLE III

SIMPLE COEFFICIENTS OF CORRELATION BETWEEN MEASURED PROPERTIES OF BISCUIT SHORTENINGS

Quantities correlated	Saponification No.	Iodine No.	Smoke point	Refractive index	Melting point	Swift stability
Iodine No.	.11	—	—	—	—	—
Smoke point	−.52*	−.01	—	—	—	—
Refractive index	.11	.77**	.14	—	—	—
Melting point	−.17	−.09	.12	.11	—	—
Swift stability	−.30	−.63**	.16	−.61**	−.10	—
Log mean peroxide value†	.31	.69*	−.28	.74**	.18	−.82**

† *Twelve values; all other measurements, 17 values.*
* *Indicates 5% level of statistical significance.*
** *Indicates 1% level of statistical significance.*

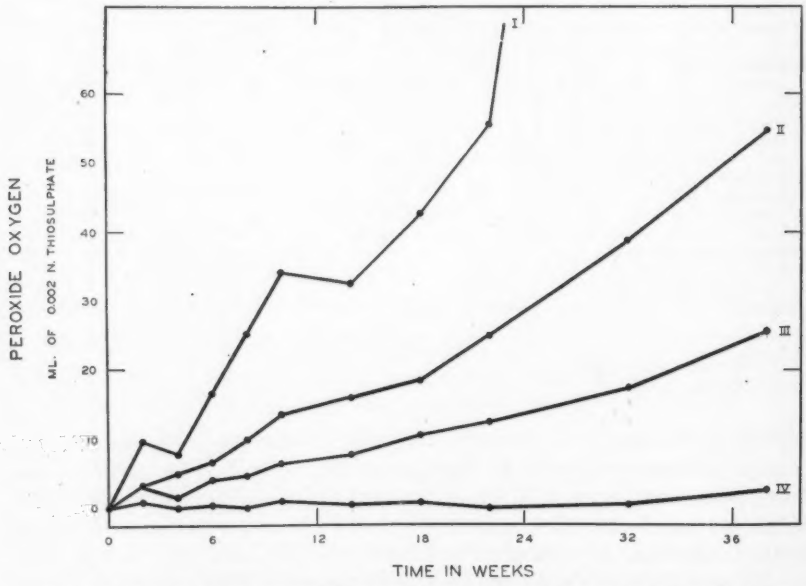

FIG. 1. *Mean peroxide oxygen development in shortenings of four types stored at 26.7° C. for 38 weeks. I, compound animal-vegetable; II, blended all-vegetable; III, hydrogenated vegetable; IV, stabilized, hydrogenated vegetable.*

The results indicate that stability was a function of shortening type. Differences in shortening stability were apparently maintained during storage (Fig. 1). Stabilization of Group IV shortenings was evidently due in part to hydrogenation to a low iodine number, while the inferior keeping quality of Group I material was presumably caused by the presence of animal fat.

Biscuits

Mean values over all sampling periods for flavour, peroxide oxygen, and pH measurements on biscuits made with each of the four types of shortening are presented in Table IV.

There were no statistically significant differences in mean pH and peroxide measurements at any of the storage temperatures and no differences in flavour score of material stored at 60° C. Significant group differences in flavour score were present in biscuits stored at 43.3° C., and highly significant differences in biscuits stored at 26.7° C. The mean flavour score for Group I biscuits was lower than the means of Groups II, III, and IV for storage temperature 26.7° C., and lower than the means of Groups III and IV for storage temperature 43.3° C.

The marked inferiority in keeping quality of Group I biscuits and the lack of differentiation among the other three groups is illustrated by the flavour changes shown in Fig. 2. The effect of storage temperature on mean flavour values averaged over all shortenings is shown in Fig. 3 (Plant *A* biscuits only). It was estimated that ration biscuits prepared with a good grade of hydrogenated vegetable shortening had average storage lives of 84, 22, and 13 weeks at 26.7° C., 43.3° C., and 60° C., respectively.

The chemical measurements yielded only limited information about keeping quality. Pronounced peroxide oxygen development was found only in biscuits prepared with compound animal–vegetable and blended all-vegetable shortenings and stored at 26.7° C. (Fig. 2). There was an initial decline in pH which was much more rapid at the higher storage temperatures (Fig. 3).

Association between mean biscuit flavour and mean peroxide oxygen content of stored shortening was negative, and closer for the lower biscuit storage temperatures (Table V). The relation between peroxide oxygen values for biscuits and for stored shortenings was not significant.

Mean biscuit flavour at 26.7° C. did not increase appreciably with the use of shortenings having Swift stabilities greater than 40 hr. at 110° C. (Fig. 4). A similar relation for Swift stability of shortenings and mean peroxide oxygen content of biscuits held at 26.7° C. is also shown in Fig. 4. Shortening stability and biscuit flavour score were more markedly associated at the lower storage temperatures (Table V). Log Swift stability and mean biscuit peroxide value at 26.7° C. were also related.

Useful storage life of the biscuits was held to be at an end when the flavour score fell to five palatability units (5). Estimated storage lives of the various

TABLE IV

MEAN VALUES OVER ALL SAMPLINGS FOR FLAVOUR SCORES, AND pH AND PEROXIDE OXYGEN VALUES OF RATION BISCUITS STORED AT 26.7°, 43.3°, AND 60° C., FOR 82, 48, AND 30 WEEKS, RESPECTIVELY

Biscuit group	No. of samples in group		Flavour score				pH				Peroxide oxygen value, ml. of 0.002 thiosulphate per gm. of fat			
			Plant *A*			Plant *B*	Plant *A*			Plant *B*	Plant *A*			Plant *B*
	Plant *A*, 60° C.	All others	26.7° C.	43.3° C.	60° C.	60° C.	26.7° C.	43.3° C.	60° C.	60° C.	26.7° C.	43.3° C.	60° C.	60° C.
I. Compound animal-vegetable shortenings	4	3	4.9	4.6	5.3	5.5	8.1	7.7	7.2	7.6	23.3	7.3	1.5	0.3
II. Blended vegetable shortenings	2	2	6.2	5.1	5.3	5.7	7.9	7.5	7.2	7.5	31.8	6.9	1.4	0.2
III. Hydrogenated vegetable shortenings	6	3	6.1	5.7	5.5	5.8	7.9	7.6	7.2	7.5	10.5	1.7	0.3	0.1
IV. Stabilized, hydrogenated vegetable shortenings	5	4	6.4	5.8	5.4	5.7	8.0	7.6	7.2	7.5	3.3	1.1	0.4	0.1
Smallest necessary difference between any two groups for statistical significance (5% level)			0.8	0.9	—	—	—	—	—	—	—	—	—	—

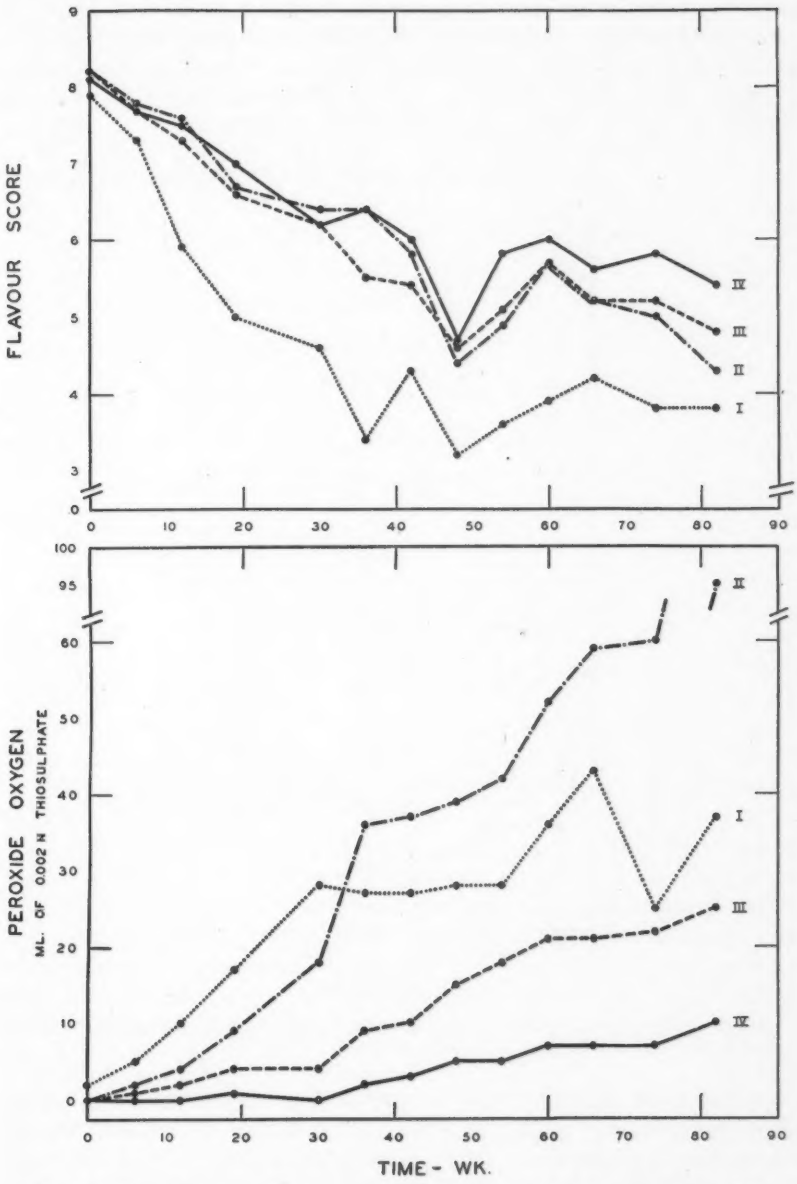

FIG. 2. *Changes in mean flavour score and peroxide value for biscuits stored at 26.7° C. and prepared with four shortening types: I, compound animal–vegetable; II, blended all-vegetable; III, hydrogenated vegetable; IV, stabilized, hydrogenated vegetable.*

groups of biscuits under the storage conditions studied are given in Table VI. Calculations based on these data supported the previous conclusions, namely, that a high level of biscuit keeping quality was obtained by the use of a reasonably stable shortening, but further increase in biscuit life was not obtained by the use of shortenings of still greater stability.

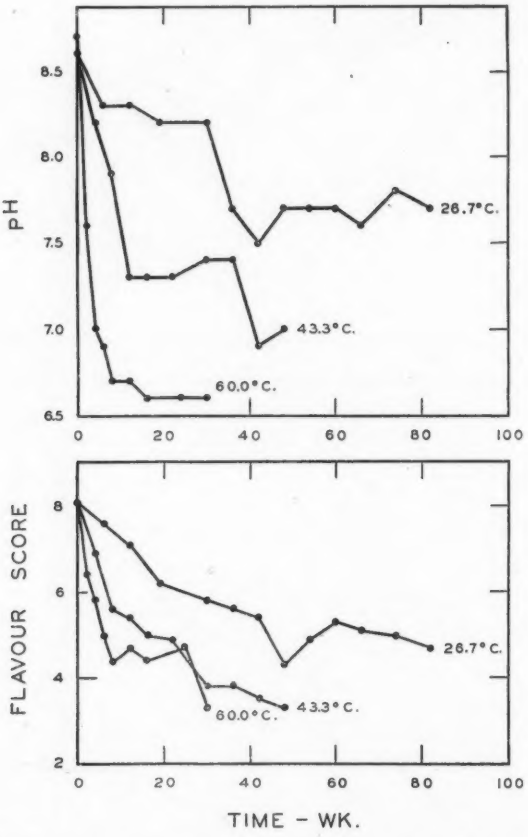

FIG. 3. *Changes in mean flavour score and pH value, over all shortenings used, for biscuits stored at 26.7°, 43.3°, and 60.0° C. (Plant A only).*

No conclusion could be drawn regarding plant practice, as the storage temperature (60° C.) at which the two plant products were compared was the one at which differentiation among biscuit groups was least pronounced. The use of different quantities of baking soda (8, 10) and the variation found in fat concentration (5), together with differences in processing procedure, probably accounted for differences between the plant products.

TABLE V

CORRELATION OF SHORTENING STABILITY WITH BISCUIT STABILITY

Quantities correlated			Correlation coefficient
Mean peroxide values of 12 stored shortenings (26.7° C.) with:			
Plant *A*	Mean biscuit flavour,	26.7° C.	−.92**
		43.3° C.	−.74**
		60° C.	−.55*
	Mean biscuit peroxide value,	26.7° C.	.53
Plant *B*	Mean biscuit flavour,	60° C.	−.56*
Log Swift stability (110° C.) of 12 shortenings with:			
Plant *A*	Mean biscuit flavour,	26.7° C.	.78**
		43.3° C.	.81**
		60° C.	.56*
	Mean biscuit peroxide value,	26.7° C.	−.78**
Plant *B*	Mean biscuit flavour,	60° C.	.21

* *Indicates 5% level of statistical significance.*
** *Indicates 1% level of statistical significance.*

Discussion

Shortenings

Mean iodine numbers of 75.2 for 11 samples of mixed animal–vegetable shortening, 78.2 for 31 samples of blended all-vegetable shortening, and 69.9 for 60 samples of hydrogenated vegetable shortening have been reported (2). These figures are somewhat higher than those reported here. An examination of smoke points determined by other workers (14) shows a comparable average of 422° F. for 10 vegetable shortenings.

None of the correlations estimated was sufficiently close for prediction purposes, although a number of anticipated associations were found. An association of melting point with iodine value was not expected in a selection of shortenings differing so widely in composition. Decrease in smoke point with increase in saponification value may have been due to variation in free fatty acid content (7, vol. 1, p. 394) or variation in content of component acids of low molecular weight (3, p. 68).

Biscuits

The investigation demonstrated that values for chemical measurements and flavour tests obtained for ration biscuits stored at the usual temperature of 60° C. (6, p. 125) may be misleading if they are used to predict storage behaviour at lower temperatures.

An explanation of the low peroxide value of extracted fat at the higher storage temperatures is possible if it is assumed that breakdown of peroxides

proceeded simultaneously with their formation, and that the relative rate of peroxide decomposition was greater at the higher temperatures. The more rapid initial decline in pH at the higher temperatures would support this, if the lowering of pH was entirely due to formation of free fatty acids from

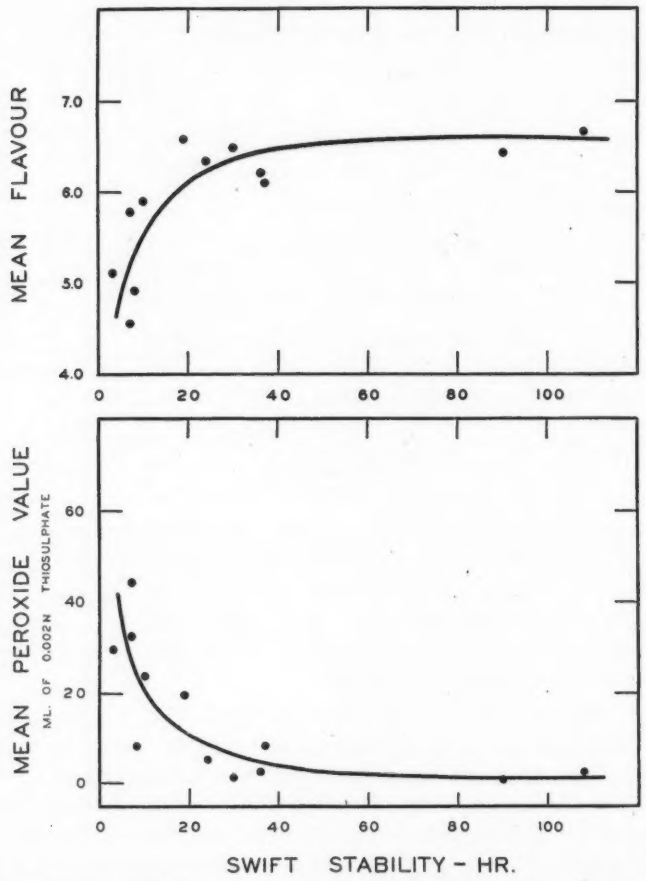

FIG. 4. *Relation of Swift stability (110° C.) of shortenings to mean flavour score and mean peroxide value of biscuits stored at 26.7° C.*

peroxide breakdown. However, pH changes might be attributable in part to changes in protein constituents, and it is also possible that decomposition products of proteins inhibited peroxide formation in the fat fraction, particularly at 60° and 43.3° C. Baking operations and the influence of non-fat constitutents in the biscuit were apparently responsible for the lack of close association between peroxide oxygen values of shortenings stored at

TABLE VI

ESTIMATED MEAN STORAGE LIFE (TIME FOR FLAVOUR SCORE TO REACH A VALUE OF FIVE) OF RATION BISCUITS STORED AT 26.7°, 43.3°, AND 60° C.

Biscuit group	No. of samples in group		Storage life, weeks			
			Plant *A*			Plant *B*
	Plant *A*, 60° C.	All others	26.7° C.	43.3° C.	60° C.	60° C.
I. Compound animal–vegetable shortenings	4	3	19	7	6	8
II. Blended vegetable shortenings	2	2	63	14	7	13
III. Hydrogenated vegetable shortenings	6	3	67	20	7	17
IV. Stabilized, hydrogenated vegetable shortenings	5	4	97	23	7	17

26.7° C. and peroxide oxygen values of the same fat extracted from biscuits also stored at that temperature. Difference in peroxide development under the two conditions was most marked for the blended all-vegetable shortenings (cf. Figs. 1 and 2).

Although peroxide values for biscuits stored at 26.7° C. and prepared from compound animal–vegetable (Group I) and blended vegetable (Group II) shortenings were both high, biscuits containing the all-vegetable product were rated as having higher mean flavour. This was presumably due to the greater stability of peroxides formed in vegetable fat, as compared to those formed in animal fat, with a corresponding delay in liberation of objectionable products of peroxide breakdown (11).

Acknowledgments

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CHARACTERISTICS OF CANADIAN LARD[1]

By H. J. Lips[2]* and G. A. Grant[3]

Abstract

Mean values for measured properties of 33 samples of lard obtained from 26 packing plants across Canada were: iodine number, 58.7; saponification number, 193.9; melting point, 43.5° C.; smoke point, 382° F.; colour, 8.8Y, 1.6R; unsaponifiable matter, 0.43%; fatty acid composition: saturated, 45.6%, oleic, 44.7%, linoleic, 8.7%, linolenic, 0.6%, arachidonic, 0.4%; storage life at 26.7° C., 9.2 weeks; Swift stability, 3.5 hr.; iodimetric peroxide, 1.6 ml. of 0.002 *N* thiosulphate per gm.; ferrometric peroxide, 9.7 m.e. per kgm.; Kreis test, 9.9; Stamm test, 2.3; alpha-dicarbonyl test, 3.4; free fatty acid, 0.4%; fluorescence, 79.2. The distribution of values is shown by histograms.

Simple correlation coefficients computed between measured properties showed the following to be associated: melting point with iodine number; free fatty acid content with melting point, smoke point, and red colour; storage life at 26.7° C. with log of Swift stability and initial ferrometric peroxide, Kreis, and alpha-dicarbonyl values.

Introduction

In pre-war years there was usually a lard surplus because the housewife preferred hydrogenated vegetable shortening to the animal product. The factors that have contributed to the inferior competitive position of lard are: lack of resistance to spoilage, lack of blandness, and unsuitability for use in deep-fat frying due to a low smoke point (28, 42). However, in pastry the shortening power of lard is often superior to that of hydrogenated vegetable oils (41, 58).

In the United States, progress has been made in the development of bland lards that may be kept for extended periods without refrigeration. These products owe their desirable characteristics to special processing, including: deodorization, partial hydrogenation, addition of hardened lard "flakes", or the incorporation of antioxidants such as gum guaiac and lecithin (44, 49, 61). In Canada, although the Food and Drugs Act has been amended to permit the incorporation in lard of certain antioxidants, commercial stabilization under the Act has not begun. Provided that additions are indicated on the container and that not more than 0.2% of stabilizing material is added, singly or in combination, the following substances may now be used: gum guaiac; vegetable oil containing tocopherols; lecithin; citric, tartaric and ascorbic acids (12).

Formerly Canada imported over 50% of her fats and oils requirements, exclusive of butter (35). During the war, the lard industry expanded, owing to a large increase in hog production and to emergency salvage and carcass

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trimming operations. It is expected that there will be an eventual surplus of lard, and one of the problems confronting the Canadian packing industry will be the improvement of this product so that high levels of export and domestic consumption can be maintained in the face of post-war competition by shortenings prepared from vegetable oils.

As a basis for proposed work to improve the quality of Canadian lard, it was considered advisable to determine the characteristics of the product as freshly produced. Surveys of Canadian lard were conducted as early as 1888 by the Food and Drugs laboratory (then a branch of the Department of Inland Revenue), but these were concerned only with adulteration of lard in respect to other fats and excess moisture (30).

A preliminary examination of market samples obtained in the city of Ottawa in the summer of 1944 showed an average keeping time of only five weeks at 26.7° C. With this indication of stability as a guide a more extensive survey of available commercial products was begun in September, 1944. Questionnaires concerning plant practice were submitted to Canadian packing houses, and representative samples of processed material were requested.

Materials and Methods

A total of 33 samples of lard was obtained from 26 packing plants across Canada and stored at −40° C. until required. Of these samples 12 were dry rendered and 21 wet rendered. As indicated in replies to questionnaires, the details of processing procedure varied considerably from plant to plant.

The product was characterized by determination of Kaufmann iodine number (14, 26); saponification number (24); capillary melting point (5); unsaponifiable matter (2); oleic, linoleic, linolenic, and arachidonic acids (9); smoke point (2); Lovibond colour (2); free fatty acid (32); and Swift stability* (27, 40). Organoleptic storage life at 26.7° C.; iodimetric and ferrometric peroxide oxygen; Kreis, Stamm, and alpha-dicarbonyl tests; and fluorescence were determined by methods reviewed elsewhere (18).

Results and Discussion

It was necessary to respect the confidential nature of some of the data obtained from the questionnaires but the majority of the laboratory results are reported (Fig. 1 and Table I). Initial odour is not given, but should be mentioned because many samples were objectionable in varying degree, having definite 'porky', 'tankage', or 'burnt' odours. Lovibond blue reading and initial iodimetric peroxide content are not represented graphically, as the results included a number of zero values. No histogram for arachidonic acid concentration is given because the variation in value was slight.

** When the indicator method (40) is used to determine Swift stability, the indicator should be renewed after the volatile fatty acids originally present have been driven off. This should not take longer than 30 min.*

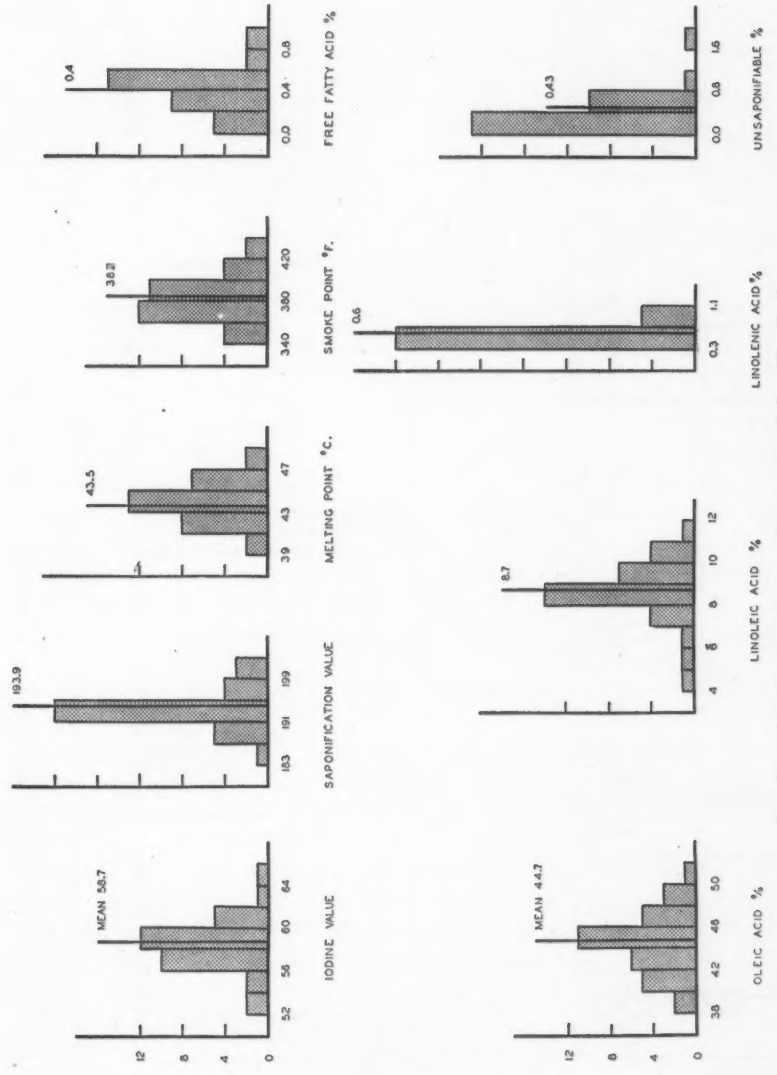

FIG. 1a. *Distribution of measured properties of Canadian lard.*

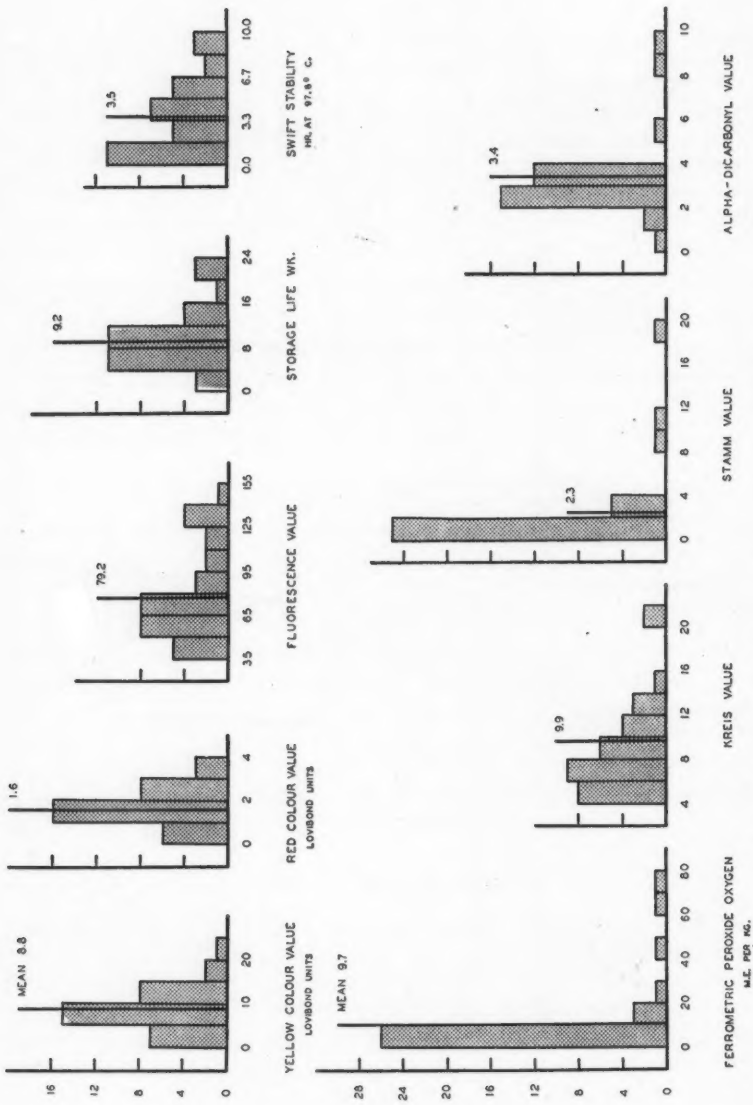

FIG. 1b. *Distribution of measured properties of Canadian lard.*

TABLE I

MEAN VALUES AND RANGES FOR MEASURED PROPERTIES OF CANADIAN LARD

Measurement	Mean	Range	Measurement	Mean	Range
Iodine number	58.7	53.1–65.3	Swift stability, hr. at 97.8 °C.	3.5	0.3–9.0
Saponification number	193.9	184.2–202.2	Ferrometric peroxide, m.e. per kgm.	9.7	0.0–73.2
Melting point, °C.	43.5	39.3–47.9	Iodimetric peroxide, ml. of 0.002 *N* thiosulphate per gm.	1.6	0.0–14.2
Smoke point, °F.	382	345–438	Kreis test, extinction coefficients	9.9	3.7–20.7
Yellow colour, Lovibond units	8.8	3.0–22.3	Stamm test, extinction coefficients	2.3	0.0–19.9
Red colour, Lovibond units	1.6	0.4–3.1	Alpha-dicarbonyl test, extinction coefficients	3.4	0.8–9.9
Blue colour, Lovibond units	0.2	0.0–1.2	Free fatty acid, as % oleic	0.4	0.1–0.9
Saturated acids*, %	45.6	—	Fluorescence, photofluorometer units	79.2	39.8–146.0
Oleic acid*, %	44.7	38.6–51.8			
Linoleic acid*, %	8.7	4.6–11.3			
Linolenic acid*, %	0.6	0.4–1.1			
Arachidonic acid*, %	0.4	0.3–0.5			
Unsaponifiable matter, %	0.43	0.20–1.70			
Storage life, weeks at 26.7° C.	9.2	2.0–22.0			

**Expressed as % of total acids.*

Characteristics of Canadian Lard

Values for iodine number, saponification number, and melting point had a fairly normal distribution (Fig. 1). Variation in these values, in the absence of adulteration or advanced spoilage, would seem to be chiefly due to differences in the original fat before processing.

There was appreciable variation in oleic, linoleic, and linolenic acid concentrations as determined spectrophotometrically. Saturated acid values were obtained by difference only. Here again the differences were concerned with the original raw materials.

Values for unsaponifiable matter vary to some extent with the method of rendering the lard, and large variations may affect the values obtained for other measurements on the whole fat (36, pp. 401, 425). The values greater than 0.8% are unusually high.

It is considered that the smoke point of lard should be at least 400° F. to compete with that of shortening, since a survey of 17 wartime shortenings, including animal–vegetable compounds, showed a mean value of 424° F. (39).

For several samples it was necessary to remove suspended material by filtration before colour measurements could be made. Blue readings were obtained for 10 of the 33 samples, and it was found that the presence of carbon in suspension markedly increased the apparent blue colour. Variation in colour would appear to be chiefly governed by factors of processing technique.

Stability of most of the lard samples was poor, as estimated by storage life at 26.7° C. and by Swift stability at 97.8° C. The magnitude of these measurements depends on the nature of the original material and the details of processing procedure, if it is assumed that no antioxidants were used.

The values for iodimetric peroxide, ferrometric peroxide, Kreis test, Stamm test, alpha-dicarbonyl test, and free fatty acid reflect the degree of exposure of the lard during processing to spoilage by biological and chemical action. Considerable variation in these respects is shown in Table I and Fig. 1. Fluorescence values were unevenly distributed.

Interrelation of Measured Properties

The literature contains a number of references to relations between various measured properties of fats and oils. Iodine value is reduced by marked oxidation (33, p. 95; 36, p. 425), saponification number is influenced to some extent by free fatty acid content (36, p. 394), and melting point is appreciably altered by changes in free fatty acid (36, p. 329). Moisture content, by affecting lard transparency, may influence estimation of the capillary melting point (17; 36, p. 288). However, according to the Canadian Food and Drugs Act (12), moisture content of lard is limited to 1%, and the product must be free from rancidity. In the absence of changes in composition, smoke point varies inversely with free fatty acid content (7; 23, pp. 132-136).

In the present study the relation of measured properties to one another was investigated by calculating simple coefficients of correlation, except where this was precluded by the presence of a large number of zero values, as in the case of iodimetric peroxide and Lovibond blue measurements. Most of the correlations proved to be insignificant; only the more important ones are reported (Table II).

Iodine number was inversely related to melting point, but no association of saponification number with other measured properties was found. The significant association of melting point with free fatty acid content indicates that the free fatty acids formed before or during processing lowered the melting point.

Smoke point, Lovibond red colour, and free fatty acid content were all interrelated. High values for free fatty acid were associated with low smoke point and high red colour. Lowering of the smoke point by free fatty acids is a well recognized effect, and significant correlations have been reported (42). The relation of free fatty acid to red colour suggests that there was a parallel increase in these two measurements during processing. Red and yellow colour readings were directly related.

The correlation of storage life at 26.7° C. with log Swift stability (Fig. 2) indicates that the latter determination has certain usefulness in the prediction of lard keeping quality at lower temperatures, at least in the absence of added antioxidants. There has been some question about this point (51). Storage life varied inversely with ferrometric peroxide, Kreis and alpha-dicarbonyl values; that is, samples with high values for these chemical measurements had short storage lives, as oxidative deterioration was already in progress. Iodine value, content of saturated and unsaturated acids and unsaponifiable matter, and fluorescence had no observed important relation to storage life. The results support a previous suggestion that degree of

unsaturation in pigs' fat is not necessarily the limiting factor in determining stability (34, pp. 60-64).

Other relations examined between measured properties were not significant.

TABLE II

COEFFICIENTS OF CORRELATION BETWEEN MEASURED PROPERTIES OF CANADIAN LARD

Quantities correlated	No. of values	Correlation coefficient
Iodine number with:		
Melting point	33	− .41*
Melting point with:		
Smoke point	33	.41*
Lovibond yellow	33	− .29
Lovibond red	33	− .24
Free fatty acid	33	− .59**
Smoke point with:		
Lovibond yellow	33	− .19
Lovibond red	33	− .38*
Free fatty acid	33	− .87**
Lovibond yellow with:		
Lovibond red	33	.82**
Lovibond red with:		
Free fatty acid	33	.41*
Storage life with:		
Log Swift stability	29	.83**
Ferrometric peroxide	26	− .63**
Kreis test	29	− .39*
Stamm test	27	− .28
Alpha-dicarbonyl test	27	− .36*

* *Indicates 5% level of statistical significance.*
** *Indicates 1% level of statistical significance.*

Relation of Measured Properties to Plant Practice

Stability and smoke point were considered likely to be altered by variations in processing procedure, so the effect of these variations upon storage life and smoke point was assessed on wet and dry rendered lards considered together and separately (Table III). However, the calculated correlation of any one plant practice with the measured properties is not strictly valid, as all other factors were not constant among plants. Moreover the calculations are based on a limited number of values, and the results may not reflect general operational experience in all cases.

A preliminary analysis of variance demonstrated no important difference in mean storage life between wet and dry rendered lard, but showed that the mean smoke point for dry rendered lard was significantly higher than for the wet rendered product. The latter result is attributable to the higher free fatty acid content of the wet rendered fats, due to their exposure to the hydrolyzing effect of long contact with steam or hot water.

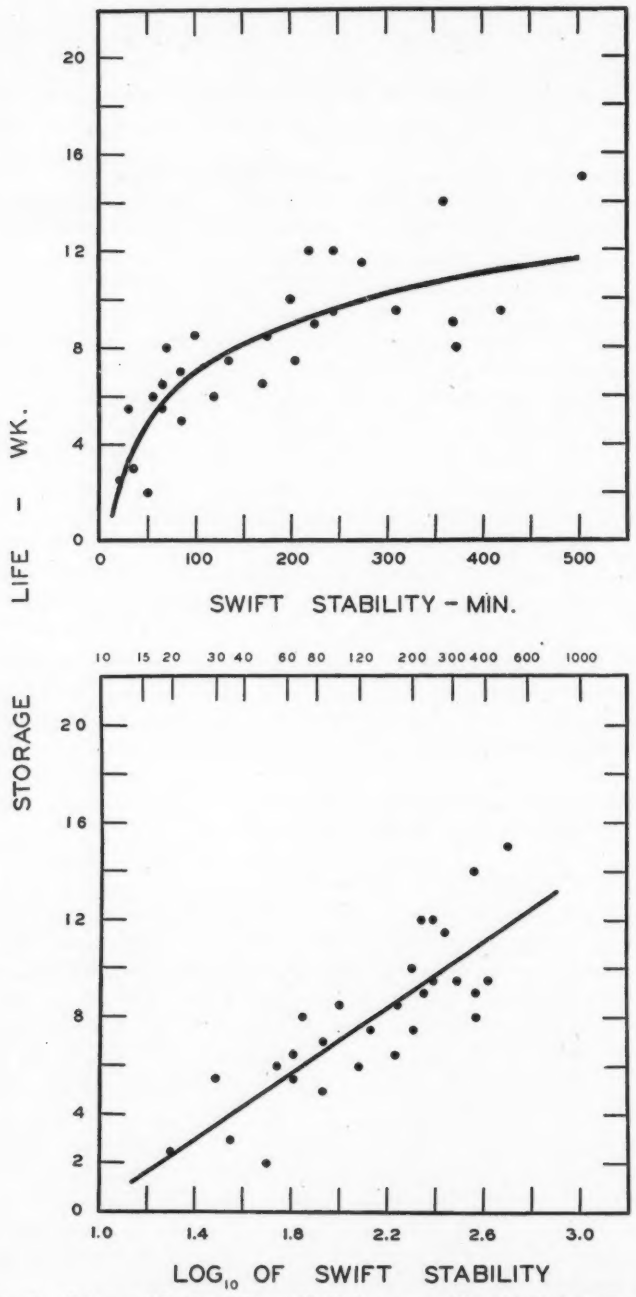

FIG. 2. *Relation of Swift stability at 97.8° C. to storage life at 26.7° C. for Canadian lard.*

TABLE III

COEFFICIENTS OF CORRELATION BETWEEN PLANT PRACTICES AND MEASURED PROPERTIES FOR CANADIAN LARD

Quantities correlated	No. of values			Correlation coefficients		
	Wet rendered lard	Dry rendered lard	Total	Wet rendered lard	Dry rendered lard	Total
Storage life with:						
Killing fat, %	21	12	33	.15	.10	.14
Cutting fat, %	21	12	33	− .14	− .35	− .23
Bones, %	21	12	33	.77**	− .15	− .22
S.P.† material, %	21	12	33	− .02	− .31	− .11
Rendering temperature	21	12	33	.41	− .30	− .12
Rendering time	3	11	14	− .42	.69*	− .02
Deodorizing temperature	—	4	5	—	.00	− .40
Deodorizing time	—	4	5	—	− .70	.08
Filtering temperature	20	11	31	− .31	− .43	− .32
Time, processing to packaging	21	12	33	.10	− .30	− .12
Smoke point with:						
Killing fat, %	21	12	33	− .77**	.52	− .19
Cutting fat, %	21	12	33	− .15	.22	− .09
Bones, %	21	12	33	.40	.53	.33*
S.P.† material, %	21	12	33	− .03	.20	.11
Rendering temperature	21	12	33	.33	.82**	.51**
Rendering time	3	11	14	.99*	− .56	− .71**
Deodorizing temperature	—	4	5	—	− .88	− .45
Deodorizing time	—	4	5	—	− .83	− .42
Filtering temperature	20	11	31	.32	− .12	− .22
Time, processing to packaging	21	12	33	− .10	.19	− .08

† *Sweet pickle.*

* *Indicates 5% level of statistical significance.*

** *Indicates 1% level of statistical significance.*

The storage life of wet rendered lard appeared to be lengthened by increase in amount of bones (Table III), presumably because of their content of natural stabilizing substances. The presence of 0.14% lecithin in pig-bone fat as compared to 0.04 to 0.06% in lard has been reported (25). With the dry rendered lard, increase in rendering time appeared to be beneficial. This may be related to better extraction of natural stabilizers from the non-fatty material. Although correlations of storage life with filtering temperature failed to attain statistical significance, they were all negative, indicating that moderately low filtering temperatures (160° to 170° F.) would be desirable for the production of more stable lard.

High smoke point was favoured by decrease in killing fat in wet rendering, and by an increase in bones. A negative correlation of smoke point with cutting fat rather than killing fat had been anticipated, since the former fat usually has more time to develop free fatty acids by enzymic action before it is rendered (23, pp. 132–136; 37, 45, 60). Similarly it was expected that

increase in bones might lower the smoke point, since these may stand for some time before rendering, with consequent development of free fatty acids in the fat that they carry. No satisfactory explanation can be offered for these discrepancies at present because of limited information about the operations concerned. The relation between smoke point and rendering temperature was positive, and between smoke point and rendering time negative. This suggests that rendering should be carried out at a relatively high temperature in as short a time as possible (23, pp. 132–136; 43, 55).

Although none of the other relations tabulated was significant, reduction in deodorizing temperatures and times used appeared to be desirable. In general the influence of processing procedures upon wet and dry rendered products was dissimilar.

Comparison with Lards from Other Countries

Extensive control examinations of lard in other countries have been reported (1, 13).

Comparative figures in the literature on the composition of lard are largely based on chemical rather than spectrophotometric measurements. For 27 American lards (4), the calculated compositions were predicated on the absence of fatty acids more unsaturated than linoleic (Table IV). However, the presence of linolenic, unsaturated C_{20-22}, and conjugated acids has been demonstrated (10; 31; 21, pp. 80–86). The presence of arachidonic acid is used as the basis of a spectrophotometric method for distinguishing between lard and hydrogenated vegetable oils (6). The greater unsaturation of other lards as compared to Canadian lards is undoubtedly due in part to differences in the nature and fat content of the diet of the hog (33, pp. 17–26). Changes in the diet similarly affect melting point, but have less effect on saponification number.

Comparative figures for lard colour have not been found in the literature. Authentic blueness in lard is said to be due to a natural pigment, and is considered an indication of careful processing rather than poor handling.* The blue pigment is unstable, and on oxidation it changes to red, or a mixture of red and yellow (23, pp. 157–158). Its presence is objectionable, since the consumer prefers whiteness.

The smoke point figure quoted in Table IV for American samples does not include the value given for a bland lard (59).

Available figures for small numbers of American samples indicate that lard usually has indifferent keeping quality unless it is stabilized by the addition of antioxidants, or subjected to special processing treatments (50).

The use of fluorescence in the study of fats to detect impurities and deterioration has been suggested by several workers (19, 20, 47, 54) but no recent data are available for comparison. Fluorescence in lard is said to depend both on state of preservation and manner of processing (8, 16, 48, 53).

* *Anon. National Provisioner, 112(20): 15. 1945.*

TABLE IV

A COMPARISON OF VALUES FOR MEASURED PROPERTIES OF CANADIAN LARD WITH OTHER REPORTED AND RECOMMENDED VALUES

Measurement	Comparative values			
	Canadian		American	Other
	Mean	Range		
Iodine number	58.7	53.1–65.3	27 samples, 64.6 (4) Recommended, 46–70 (3)	General, 46–66 (22, p. 136) English, 108 samples, 57–73 (56) Portuguese, 30 samples, 63.9 (46)
Saponification number	193.9	184.2–202.2	Recommended, 195–202 (3)	General, 193–200 (22, p. 136) Portuguese, 30 samples, 195.8 (46)
Melting point, °C.	43.5	39.3–47.9	—	General, 28–48 (22, p. 136)
Smoke point, °F.	382	345–438	6 samples, 371 (59)	—
Saturated acids*, %	45.6	—	27 samples, 36.8 (4)	Portuguese, 30 samples, 38.5 (46)
Oleic acid*, %	44.7	38.6–51.8	27 samples, 51.5 (4)	Portuguese, 30 samples, 49.2 (46)
Linoleic acid*, %	8.7	4.6–11.3	27 samples, 11.7 (4)	Portuguese, 30 samples, 12.5 (46)
Arachidonic acid*, %	0.4	0.3–0.5	0.02–0.21 (15) 0.31–0.40 (11) 0.2 –0.6 (6)	
Unsaponifiable matter, %	0.43	0.20–1.70	Recommended, 1.0 max. (3)	General, 0.2–0.4 (22, p. 136; 29, p. 135) Portuguese, 30 samples, 0.14 (46)
Swift stability, hr. at 97.8 °C.	3.5	0.3–9.0	7 samples, 5.3 (50)	Other Canadian, 14 samples, 2.2 (38, 40)
Iodimetric peroxide, ml. of 0.002 *N* thiosulphate per gm.	1.6	0.0–14.2	4 samples, 1.5 (28) 6 samples, 0.7 (52) Recommended, 2.5 ml. max. (3)	—
Free fatty acid, as % oleic	0.4	0.1–0.9	6 samples, 0.26 (59) 5 samples, 0.29 (28) 3 samples, 0.33 (57) 4 samples, 0.35 (28) Recommended, 1% max. (3)	General, 0.2–0.7 (22, p. 136)

* *Expressed as % of total acids.*

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STUDIES COMPARING THE SANITIZING EFFICIENCIES OF HYPOCHLORITES AND QUATERNARY AMMONIUM COMPOUNDS[1]

By C. K. Johns[2]

Abstract

The germicidal speed of four quaternary ammonium compounds has been compared with that of two hypochlorites against *Staphylococcus aureus*, *Bacillus panis* (vegetative cells and spores), *Micrococcus candidus*, cheese starter organisms, *Escherichia coli* and *Pseudomonas aeruginosa*, using the glass slide technique originally devised for comparing chlorine sterilizing agents. Against the Gram-positive species, the quaternary compounds were generally more effective than the hypochlorites; against the Gram-negative species, the reverse held true. Cheese starter organisms were an exception, being killed faster by the hypochlorites. Three of the four quaternary compounds were closely comparable in efficiency, while the fourth was definitely slower. The hypochlorites responded much more readily to favourable adjustments in pH and temperature than did the quaternary compounds. Some bacteriostatic effect was observed with higher concentrations of all four quaternary compounds, but it is not believed that the results were significantly affected thereby. The glass slide technique appears to offer many advantages in the evaluation of the germicidal efficiency of products designed for sanitizing metal or glass surfaces in food processing plants.

Introduction

During the past decade, a large number of 'surface active' detergents have been developed. Of these, the quaternary ammonium compounds have been reported to be particularly effective as germicides (2, 8, 9, 10, 12, 13, 23, 27). Among other uses they are being recommended to supplant hypochlorites for the sanitizing of equipment in the dairy and food industries. So far, however, the only direct comparison of their effectiveness with that of hypochlorite has been reported by Jamieson and Chen (14) in the sanitizing of milk cans. Unfortunately the quaternary compounds were employed at a much higher concentration than the hypochlorite, rendering comparisons difficult. The present studies were designed to afford a direct comparison between representatives of both types of germicide.

In the sanitizing of washed food-handling equipment, the bacteria present on the surfaces of such equipment are often protected by a slight film of diluted milk or other organic material. Tests conducted along the lines of the conventional phenol coefficient determination, in which the test organisms are freely suspended in a solution of the product under test, do not even remotely approximate the conditions under which the sanitizing agent must work in practice. To overcome this objection, when studying the comparative germicidal efficiency of chlorine compounds (19, 20), a 'glass slide' technique was evolved in which the test organisms were present in a partially dried film of diluted skim-milk on the surface of a microscopic slide. This

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technique had shown satisfactory reproducibility with chlorine products, hence it was decided to use it, with slight modifications, to compare the germicidal efficiencies of hypochlorites and quaternary ammonium compounds.

In the previous studies with chlorine compounds, the F.D.A. 209 strain of *Staphylococcus aureus* was selected as the principal test organism, since it had been found (18) to be much more resistant to chlorine compounds than Gram-negative organisms such as members of the coliform group. However, in view of the reported specificity displayed by surface-active agents (24) other bacteria of interest to the food industry were included in the present studies.

The importance of testing germicides in the concentrations at which they will be employed has been pointed out (19, 26). This has been borne in mind in the present studies. In addition, the period of contact with the germicide is of considerable practical importance. While in the sanitizing of vats, pipelines, coolers, etc., a contact period of several minutes can generally be allowed, in other instances, as in the treatment of farm dairy utensils, egg breaking sets, etc., the contact period often varies from an instantaneous dip to perhaps 10 sec. With this in mind, attention has been concentrated upon the ability of the products under test to bring about effective bacterial destruction within 1, 5, 10, or 20 sec.

Experimental

A 20 to 24 hr. growth of the F.D.A. strain of *S. aureus* on nutrient agar was washed off and suspended in sterile distilled water. After filtration through a No. 1 Whatman paper to remove clumps of organisms, the suspension was standardized to give a plate count of approximately 200,000,000 per ml. One millilitre of suspension was then introduced into 60 ml. of a 1 : 10 dilution of sterile skim-milk. The container for the inoculated skim-milk was of such dimensions that the depth of the liquid was 1½ in.

A previously sterilized slide was taken with sterile slide forceps and dipped into the seeded skim-milk suspension so that the lower half of the slide—an area of 1 by 1½ in. on either side—was immersed. The slide was withdrawn, carefully drained against the rim of the container for approximately 10 sec. to remove surplus liquid, then placed on end on a pad of sterile filter paper in a specially constructed draining can. A sufficient number of slides to run the desired number of tests on a given dilution of a product—usually four or five—were prepared consecutively, following which the tests were carried out before the films of diluted skim-milk had dried over more than 25% of the area. (Tests with slides allowed to dry completely give a significantly different picture.)

Previous to preparing the slides, 100 ml. portions of the solutions to be tested were placed in 100 ml. beakers and brought to the desired temperature. The slide first treated was then drained of any excess liquid on the filter paper layers in the draining can, dipped into the test solution, and gently agitated for the required period. At the end of the period it was quickly removed, dipped momentarily in a beaker of tap water (to minimize bacteriostatic

action by the adhering germicide), shaken once to remove excess liquid, placed in a Petri dish, and the plate immediately poured with tryptone glucose agar containing 7.5% sodium chloride to inhibit contaminants (3, 22). Plates were counted after incubation at 37° C. for 48 hr. The remaining slides were similarly treated in correct sequence.

To obtain some idea of the number of organisms present on the slides before treatment with the germicide, control plates were prepared at regular intervals during each day's run by dipping sterile slides into a second container of diluted skim-milk in which the concentration of test organisms was only 1/60 to 1/600 of that of the original suspension. These slides were drained in the usual manner, then dipped in tap water before plating. The average colony count on these control slides, multiplied by the appropriate factor, reflected the approximate number of organisms present on the regular slides before treatment. By dividing this figure by 1000, a value was obtained indicating the number of organisms remaining after 99.9% had been destroyed. This was taken as the end-point in comparing the efficiency of the various products. Although the experimental error is obviously large when dealing with short exposure periods, the end-points obtained have shown far better agreement between replicate runs than has been obtained with various modifications of the F.D.A. method of determining the phenol coefficient.

The products tested were selected as being fairly representative of those on the market in Canada, and included:

(*a*) Roccal, a 10% solution of alkyldimethylbenzylammonium chloride.

(*b*) R-2-L, ditto.

(*c*) Hyamine 1622, (diisobutylphenoxyethoxyethyl)dimethylbenzylammonium chloride in crystalline form.

(*d*) Emulsept, a 10% solution of *N* (acylcolaminoformylmethyl) pyridinium chloride.

(*e*) Dalglish Liquid Bleach, a liquid sodium hypochlorite product containing about 12% available chlorine.

(*f*) Klenzade X4, a newer liquid sodium hypochlorite, said to be buffered to lower the pH and to render it more stable.

Results

SERIES I. *S. aureus*

To conserve space in presenting data, the average time required to reach the end-point (99.9% destruction) has been calculated for each dilution of each product. Table I shows that Roccal, R-2-L, and Hyamine 1622 possessed similar germicidal speed; Emulsept, on the other hand, was somewhat slower.

Although the Dalglish hypochlorite showed poorer agreement between the results of the two runs than did the remaining products, it appeared to be intermediate between Emulsept and the other three quaternary ammonium compounds. Klenzade X4, the second hypochlorite, was the slowest acting

TABLE I

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF *S. aureus* AT 20° AND 45° C.

Compound	Concentration of active ingredient, p.p.m.			
	400	200	100	50
20° C.—(average of two runs)				
Roccal		5 (6.83)	5 (7.02)	10 (7.22)
R-2-L		5 (6.95)	5 (6.81)	10 (6.5)
Hyamine 1622		5 (6.48)	5 (6.88)	10 (7.02)
Emulsept		15 (5.32)	15 (6.85)	20 (7.02)
Dalglish	7.5 (10.8)	12.5 (10.48)	15 (9.98)	
Klenzade X4	>20 (11.02)	>20 (10.76)	>20 (10.2)	
45° C.				
Roccal		1	5	5
R-2-L		1	5	5
Hyamine 1622		1	5	5
Emulsept		10	5	10
Dalglish	1	1	5	
Klenzade X4	1	5	10	

N.B. Figures in parentheses represent pH values at 20° C.

of all, the end-point (99.9% destruction) not being reached within 20 sec. in either run.

To determine whether the residual germicide on the treated slide exerted a bacteriostatic influence, an additional slide was prepared for the five second exposure with the tap-water rinse omitted. Since there was close agreement between the counts on both rinsed and unrinsed slides, it was concluded that the bacteriostasis was insignificant. Nevertheless, the dip rinse was continued as a safeguard. (In subsequent tests with spores, using higher concentrations of quaternary compounds, the value of this step became more evident.)

The Influence of pH upon Germicidal Speed

It is well known that the germicidal speed of hypochlorites is reduced as the alkalinity increases (4, 15, 19, 30, 32). It has also been reported that the reverse holds true for cationic agents such as the quaternary compounds (2, 10, 13). Consequently, to determine whether differences in germicidal speed could be attributed to differences in reaction, the pH values for the various solutions were determined, using a Beckman pH meter. With the hypochlorites no attempt has been made to correct the readings for the alkaline salt errors (7); the actual differences between the two products are probably greater than those suggested by these readings.

The results (Table I) suggest that the superiority of Dalglish over Klenzade X4 was due to the lower alkalinity of the former. The more acid reaction of Emulsept at 200 p.p.m. might explain its slower action, but this would not apply in the 100 and 50 p.p.m. concentrations. To assess more directly the influence of pH, a second series of tests was conducted in which representative products were run at two different pH levels. These levels were obtained by substituting one-quarter strength buffer solutions of pH 6 and 10 (prepared from tablets manufactured by the Coleman Electric Co.*) for distilled water in preparing working dilutions of representative products. The results, together with the pH values obtained on the solutions immediately following the germicidal tests, appear in Table II.

TABLE II

GERMICIDAL POTENCY OF VARIOUS SANITIZING AGENTS AGAINST *S. aureus*, AT 20° C. AS INFLUENCED BY pH

Product	Conc., p.p.m.	Buffer solution pH	Actual pH	Period of exposure, sec., required for 99.9% destruction
Roccal	200	6	6.24	5
	100		6.20	5
	100	10	9.86	5
	50		9.90	20
	25		9.90	20
Emulsept	200	6	6.20	20
	100		6.19	20
	100	10	9.90	10
	50		9.90	20
	25		9.90	40
Klenzade X4	100	6	7.26	1
	50		6.82	1
	25		6.48	5
	400	10	10.49	5
	200		10.15	5
	100		9.98	40

While adjustment to a more alkaline level had little or no effect on the germicidal speed of Roccal and Emulsept, that obtained from the adjustment of Klenzade X4 to a less alkaline reaction was quite striking. Here a 25 p.p.m. concentration prepared from a pH 6 buffer solution showed fewer surviving organisms after a one second exposure than did 400 p.p.m. prepared from a pH 10 buffer solution. Comparisons with the results in Table I also show the greater activity of Klenzade X4 solutions prepared from the pH 10 buffer solution compared with those prepared without any adjustment of pH.

* *The pH 6 buffer was composed of potassium acid phthalate and sodium phosphate; the pH 10 buffer of sodium tetraborate and sodium carbonate.*

At both pH levels Emulsept killed more slowly than Roccal, suggesting that the difference noted must be due to some factor other than the hydrogen ion concentration.

The Influence of Temperature Upon the Germicidal Speed

With hypochlorites, germicidal efficiency is significantly increased as the temperature of the solution is raised (4, 5, 18, 30, 32). In the sanitizing of egg breaking equipment, as well as of larger items of equipment in the food and dairy industries, it is frequently feasible to use warm or hot solutions of germicide. To determine the effect of higher temperatures in increasing the activity of both quaternary ammonium and hypochlorite solutions, a further series of tests was conducted at 45° C., this being the highest temperature found to be borne comfortably by the workers' hands.

The results (lower half of Table I) show a slight but distinct increase in germicidal speed of quaternary ammonium compounds when their temperature was raised from 20° to 45° C. This increase, however, was insignificant compared with that shown by the two hypochlorite products; with them, the germicidal efficiency was strikingly enhanced, so that 100 p.p.m. at 45° C. was considerably more effective than 400 p.p.m. at 20° C.

SERIES II. *Micrococcus candidus*

In view of current interest in thermoduric bacteria in market milk, a culture of a micrococcus (later identified as *M. candidus*) that had resisted laboratory pasteurization was obtained from Mr. A. Moldavan of the Guaranteed Pure Milk Company, Montreal. Using standard agar (1) four sets of tests were run with this organism at 20° C., the average of the results from three of which appear in Table III.

In the first set, the hypochlorites appeared to have a slight advantage in speed. However, when the second run was made some four weeks later, they appeared distinctly slower. Two further runs were made, in each of which the results favoured the quaternary compounds. No reason for this discrepancy could be discovered.

A single run was made at 45° C. The results (Table III) again indicate that higher temperatures enhance the efficiency of hypochlorites to a much greater extent than they do that of the quaternary compounds.

SERIES III. *Bacillus panis*

Since considerable importance is attached to the presence of spore-forming organisms in certain branches of the food industry, a strain of *B. panis*, isolated from ropy bread, was included in these studies.

In the first set of tests, to obtain spore forms the growth on 10-day-old cultures was washed off, standardized, rapidly heated to boiling in a water-bath to destroy vegetative forms, and again cooled before being used. In the second set, where vegetative organisms only were desired, poured plates received a surface inoculation from material picked from the margins of day-

old colonies; the plates were incubated at 32° C. for 17 hr., the growth suspended, and standardized. After preparing the skim-milk dilutions for the test run, the remainder of the suspension was momentarily heated to boiling. Subsequent plating showed it to have contained approximately three spores per million vegetative cells.

TABLE III

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF *M. candidus*, AT 20° AND 45° C.

Compound	Concentration of active ingredient, p.p.m.		
	200	100	50
20° C. (average of three runs)			
Roccal	5	5	10
R-2-L	5	5	10
Hyamine 1622	5	5	13
Emulsept	7	10	20
Dalglish	>20	>20	>20
Klenzade X4	>20	>20	>20
45° C.			
Roccal	5	5	5
R-2-L	5	5	5
Hyamine 1622	5	5	5
Emulsept	5	10	10
Dalglish	5	5	5
Klenzade X4	5	10	10

Owing to the spreading nature of the colonies, counting of plates was rather difficult. In an endeavour to improve the situation in the test run with the vegetative cells, the agar content of the medium (1) was raised to 2.5%. While this proved helpful, counting was still more difficult than with the other organisms studied.

The results of the two tests with spore suspensions of *B. panis* (Table IV) suggest that three of the quaternary ammonium compounds were decidedly more effective against spores than were the hypochlorites. However, the more favourable showing of the quaternary ammonium compounds may be partly due to the inhibitory influence of the higher concentrations of germicide adhering to the slide even after the slide had received a dip rinse. This will be discussed in a later section.

The single test carried out against the vegetative cells of *B. panis* (Table IV) revealed an entirely different picture. Here the superiority shown by the quaternary compounds against the spore forms is no longer evident. Both hypochlorites showed far greater activity against the vegetative cells than against the spores.

TABLE IV

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF SPORES AND OF VEGETATIVE CELLS OF *B. panis*, AT 20° C

Compound	Concentration of active ingredient, p.p.m.				
	1000	400	200	100	50
Spores (average of two runs)					
Roccal	3	15	>20		
R-2-L	1	10	>20		
Hyamine 1622	1	>20	>20		
Emulsept	15	>20	>20		
Dalglish	>20	>20	>20		
Klenzade X4	>20	>20	>20		
Vegetative cells					
Roccal			5	5	5
R-2-L			5	>20	20
Hyamine 1622			1	5	5
Emulsept			5	5	10
Dalglish		1	1	5	
Klenzade X4		5	5	5	

SERIES IV. *Lactic Acid Streptococci*

The importance of the lactic acid streptococci in the dairying industry suggested the desirability of including them in these studies. To this end, a cheese starter (No. 43) currently in use at the Central Experimental Farm Dairy was selected. This starter comprises a variety of strains of lactic acid streptococci and aroma-producing organisms, and is fairly representative of the types of organisms that might be encountered in shipping cans in which whey had been returned from the factory. In order to preserve the quantitative relation between the various strains in the starter, it was deemed best to use a milk culture of starter, incubated at 21° C. for 22 hr., to inoculate the skim-milk diluent, rather than culturing on laboratory media and standardizing the suspension in the usual manner. On the basis of preliminary trials, the starter was diluted with sterile skim-milk to give a plate count of approximately 200,000,000 per ml. Since the majority of the organisms formed chains of varying length, the number of cells present was actually far in excess of that indicated by the plate count. Plates were poured with Bacto whey agar with the addition of 1.0% yeast extract, and incubated at 32° C. for 72 hr.

The results from the first run showed a surprising lack of resistance to both types of germicide. For the second run, therefore, the concentrations of germicides were cut in half. Although all six products were very effective, the hypochlorites had some advantage at all three concentrations tested (Table V).

SERIES V. *Escherichia coli*

In view of the widespread use of the coliform test as a check on the adequacy of sanitizing procedure in milk pasteurization plants, studies with this organism seemed particularly appropriate. Difco Violet Red Bile Agar was used as the plating medium, and counts were made after 20 hr. incubation at 37° C.

TABLE V

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF CHEESE STARTER ORGANISMS AT 20° C. (AVERAGE OF TWO RUNS)

Compound	Concentration of active ingredient, p.p.m.		
	100	50	25
Roccal	5	5	10
R-2-L	3	5	10
Hyamine 1622	3	8	20
Emulsept	3	8	10
Dalglish	1	1	5
Klenzade X4	1	5	5

The data in Table VI indicate that the quaternary ammonium compounds were less effective here than they were against *S. aureus*. This is in contrast to the hypochlorites, which are generally most active against Gram-negative organisms (15, 16, 19).

TABLE VI

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF *E. coli*, AT 20° AND 45° C.

Compound	Concentration of active ingredient, p.p.m.				
	400	200	100	50	25
20° C. (average of two runs)					
Roccal		15	20	>20	
R-2-L		10	>20	>20	
Hyamine 1622		>20	>20	>20	
Emulsept		15	>20	>20	
Dalglish	1	1	3		
Klenzade X4	1	1	3		
45° C.					
Roccal			5	5	>20
R-2-L			5	10	10
Hyamine 1622			5	20	>20
Emulsept			5	10	>20
Dalglish			1	1	5
Klenzade X4			1	5	5

The Influence of pH upon Germicidal Speed

As with *S. aureus*, a series of tests was carried out on representative products diluted to working concentration with buffer solutions. The results (Table VII) again showed only a very slight stepping-up of potency of the quaternary

TABLE VII

GERMICIDAL POTENCY OF VARIOUS SANITIZING AGENTS AGAINST *E. coli* AT 20° C. AS INFLUENCED BY pH

Product	Concentration, p.p.m.	Buffer solution pH	Actual pH	Period of exposure (sec.) required for 99.9% destruction
Roccal	200	6	6.18	10
	100		6.11	20
	100	10	9.25	10
	50		10.00	>20
R-2-L	200	6	6.35	10
	100		6.35	20
	100	10	10.25	10
	50		10.25	20
Emulsept	200	6	6.00	>20
	100		6.01	>20
	100	10	9.96	20
	50		9.99	>20
Klenzade X4	50	6	6.72	1
	25		6.40	5
	10		6.25	5
	200	10	10.30	1
	100		10.11	1
	50		10.01	5

N.B. 99.9% destruction leaves 27 colonies.

compounds through the upward adjustment of pH. The activity of the hypochlorite (Klenzade X4) was greater at a lower pH value, but the effect was less than that noted with *S. aureus* (Table I).

The Influence of Temperature on Germicidal Speed

A single run made at 45° C. (Table VI) showed a slightly greater increase in effectiveness of the quaternary compounds than was noted with *S. aureus*. These compounds were, however, invariably much less effective than were the hypochlorites at the higher temperature, although the acceleration of germicidal speed of the hypochlorites was less marked than with *S. aureus*.

SERIES VI. *Pseudomonas aeruginosa*

In view of the marked resistance displayed by this organism toward various antibiotics, it was included as one of the test organisms. Plates were poured with tryptone glucose skim-milk agar (1) and incubated at 20° to 25° C. for 48 hr.

The data in Table VIII indicate that *P. aeruginosa* showed slightly less resistance than *E. coli* to the quaternary ammonium compounds, but somewhat more to the hypochlorites. Against both organisms the hypochlorites were the more effective sterilizing agents.

TABLE VIII

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF *P. aeruginosa*, AT 20° C.

(Average of two runs)

Compound	Concentration of active ingredient, p.p.m.			
	400	200	100	50
Roccal		5	10	>20
R-2-L		5	15	>20
Hyamine 1622		7.5	>20	>20
Emulsept		7.5	10	20
Dalglish	1	1	5	
Klenzade X4	1	5	5	

BACTERIOSTATIC ACTION OF QUATERNARY COMPOUNDS

When these studies were nearing completion, our attention was directed to the recent report by Klarmann and Wright (21). In a modification of the F.D.A. technique for determining the phenol coefficient of quaternary ammonium compounds, these workers used sterile glass strips 10 by 38 mm., which were placed in the 'medication tubes'. After 10 min. exposure of the test organism, the glass strip was withdrawn and plated. Where the glass strip had been immersed in a 333 p.p.m. solution of a quaternary compound, a definite area of inhibition of growth of *S. aureus* could be seen (Fig. 3 in their paper). This led us to re-examine our data to discover whether such bacteriostatic action might be influencing our results.

In the tests with spores of *B. panis*, it was noted that on the plates poured on slides treated with 1000 and 400 p.p.m. solutions of the quaternary compounds, no colonies appeared on or adjacent to the slide itself, while with the hypochlorites, the majority of the colonies were on or near the slide. A similar paucity of colonies on the slide itself where the higher concentrations of quaternary compounds were used had been noted earlier with *S. aureus*. (This effect is illustrated by Fig. 1, in which Roccal and Dalglish are compared against *M. candidus*.) The plates from slides treated with 200 p.p.m. of the quaternary compounds showed some colonies on or near the slides.

That definite bacteriostasis was occurring with the higher concentrations of the quaternary compounds was confirmed by various methods, including the plating of sterile slides dipped directly into the quaternary solution, then subjected to rinsing treatments varying from a quick dip to 20 sec. in length. The plates were poured with agar medium heavily seeded with the test organism. These tests showed some growth inhibition with all three Gram-positive organisms tested (*S. aureus*, *B. panis*, and *M. candidus*) while the Gram-negative organisms (*E. coli* and *P. aeruginosa*) failed to show any such effect. The results from the most comprehensive series of tests are shown in Table IX. The control (unrinsed) slides showed marked inhibition of growth with concentrations of Roccal from 1000 to 100 p.p.m. inclusive; with the dip rinse, this was confined to the 1000 and 400 p.p.m. concentrations, while with the 20 sec. rinse the inhibition was almost negligible. In Sections *D*, *E*, and *F*, an anionic compound, Fisher's Laboratory Aerosol, at 10 p.p.m. was substituted for tap water, the intention being to neutralize the effect of the cationic quaternary compound adhering to the slide. The results, however, show little evidence of such neutralization. Similar results were obtained in another set of tests in which another anionic compound, Nacconal FSNO, was also included.

TABLE IX

DEGREE OF INHIBITION BY ROCCAL. SEEDED CULTURE *S. aureus*

Treatment of slide (sterile) after dipping in Roccal	Roccal, p.p.m.				
	1000	400	200	100	50
	Degree of inhibition (++++—complete)				
A. Dip rinse, tap water	++++	+++	+	+	O
B. 5 sec. rinse, tap water	+	Slight	+	Very slight	Very slight
C. 20 sec. rinse, tap water	Very slight	Very slight	Slight	O	O
D. Dip rinse; Aerosol, 10 p.p.m.	++++	++	+	+	Slight
E. 5 sec. rinse; Aerosol, 10 p.p.m.	<+	+	Very slight	<+	Very slight
F. 20 sec. rinse; Aerosol, 10 p.p.m.	<+	<+	Slight	+	Very slight
G. No rinse, control	++++	++++	++	++	Slight

To determine whether the clear zones represented inhibition or actual killing, a bent needle was touched to areas where growth was abundant, then to clear areas. After overnight incubation at 37° C., the inoculated areas were again touched with the bent needle and transfers made to oval tube slants of tryptone glucose agar (28). These were again observed for growth after overnight incubation. Of 155 'fishings', 97 showed no growth on subculturing; where growth did occur, the site of the original 'spotting' was approaching the area of visible growth. As a further check, the bent needle was touched directly to the medium in the clear zones, then to oval tube slants. Growth took place in only 19 of 117 such 'fishings'. It would appear, therefore, that in addition to inhibition, there is actual killing of bacteria by the small amount of quaternary compound carried over on the slide. While this com-

plicates the precise evaluation of the germicidal efficiency of these compounds in the higher concentrations, from the practical standpoint it must be regarded as a distinct advantage, particularly where the period of contact with the germicide is short, as in the case of farm sanitization of dairy utensils.

An unexpected phenomenon was encountered when the tests reported in Table IX were repeated, substituting slides previously dipped in sterile diluted skim-milk for plain slides. It was expected that the film of organic matter would tend to lower both bactericidal and bacteriostatic effectiveness of the quaternary compounds. Instead, the zones of inhibition were appreciably larger than those where plain slides were used (Fig. 2). This may be due to greater adsorption and retention of Roccal by the film of milk solids. Further studies on this phase are being carried out.

The bulk of our studies on bacteriostasis were carried out with Roccal. However, the other three quaternary products have all shown a similar effect in varying degree, as illustrated in Fig. 3, where *M. candidus* was the test organism. Here are shown plates of slides that received a one-second treatment with each of the four quaternary compounds in concentrations of 200 and 100 p.p.m. respectively. Each slide received a momentary dip in tap water before being placed in the Petri dish. The order of decreasing bacteriostasis, Roccal >R-2-L>Hyamine 1622>Emulsept, has been noted in several of the regular experimental runs, the first two being definitely more inhibitory than the last two. Neither of the two hypochlorites showed any sign of bacteriostasis in concentrations up to 1000 p.p.m.

Discussion

With the exception of the plant studies reported by Scales and Kemp (32), Jamieson and Chen (14), and Krug and Marshall (23), most attempts to evaluate the germicidal efficiency of surface-active compounds have been by means of the F.D.A. technique for the determination of the phenol coefficient, or some modification thereof. The difficulty of obtaining consistent results with the F.D.A. technique in the testing of chlorine compounds (19) has been similarly reported for quaternary ammonium compounds by various workers (21, 29, 34). Aside from this, major objections to the phenol coefficient technique are that (*a*) it only indicates complete destruction of the test organisms,

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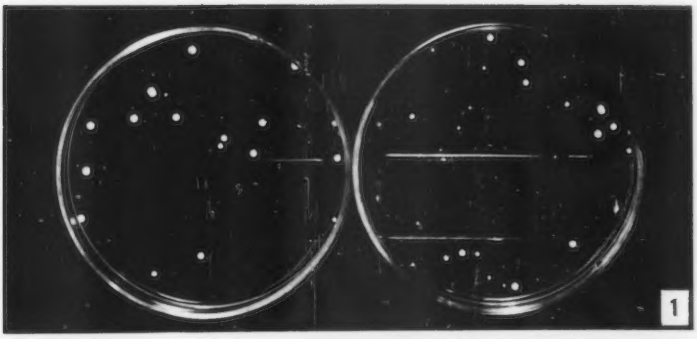
FIG. 1. *Illustrating relative scarcity of colonies on or near slide treated with Roccal 100 p.p.m. for five seconds (left-hand side), compared with one treated with Dalglish 200 p.p.m. 20 sec. (right-hand side). (M. candidus, test organism.)*

FIG. 2. *Illustrating inhibitory effect of Roccal 100 p.p.m. carried over on glass slide (S. aureus, test organism). Top pair, no rinse after treatment; centre pair, dip rinse; bottom pair, five second rinse. Plain slides on left-hand side; slides dipped in sterile 10% skim-milk on right-hand side.*

FIG. 3. *Comparative bacteriostatic effect of four quaternary compounds. One second exposure, M. candidus. (A) Roccal, (B) R-2-L, (C) Hyamine 1622, (D) Emulsept. Left-hand side = 100 p.p.m. Right-hand side = 200 p.p.m.*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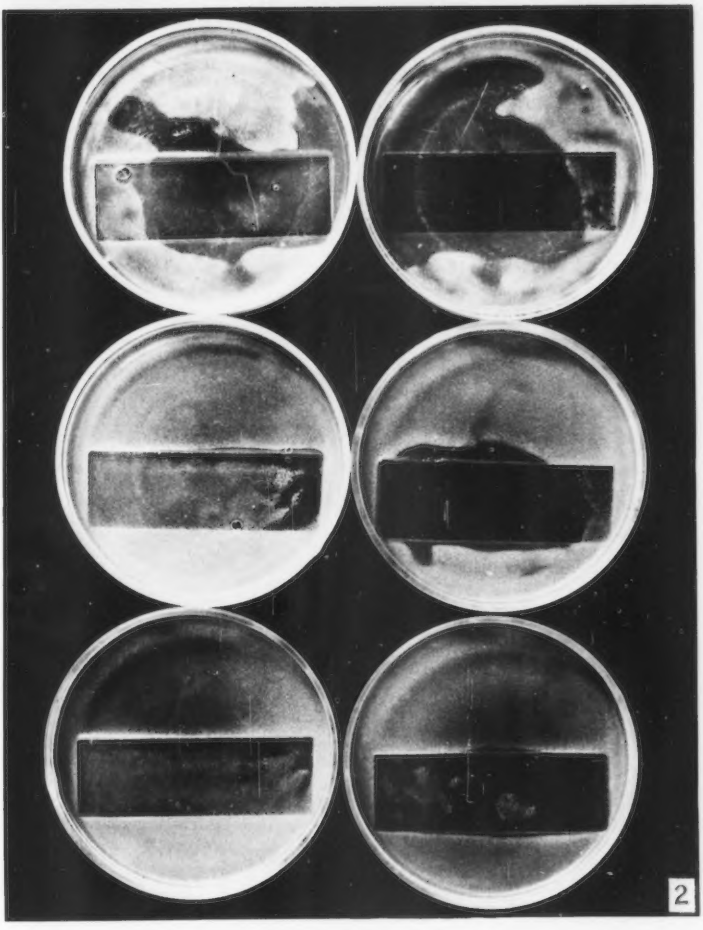
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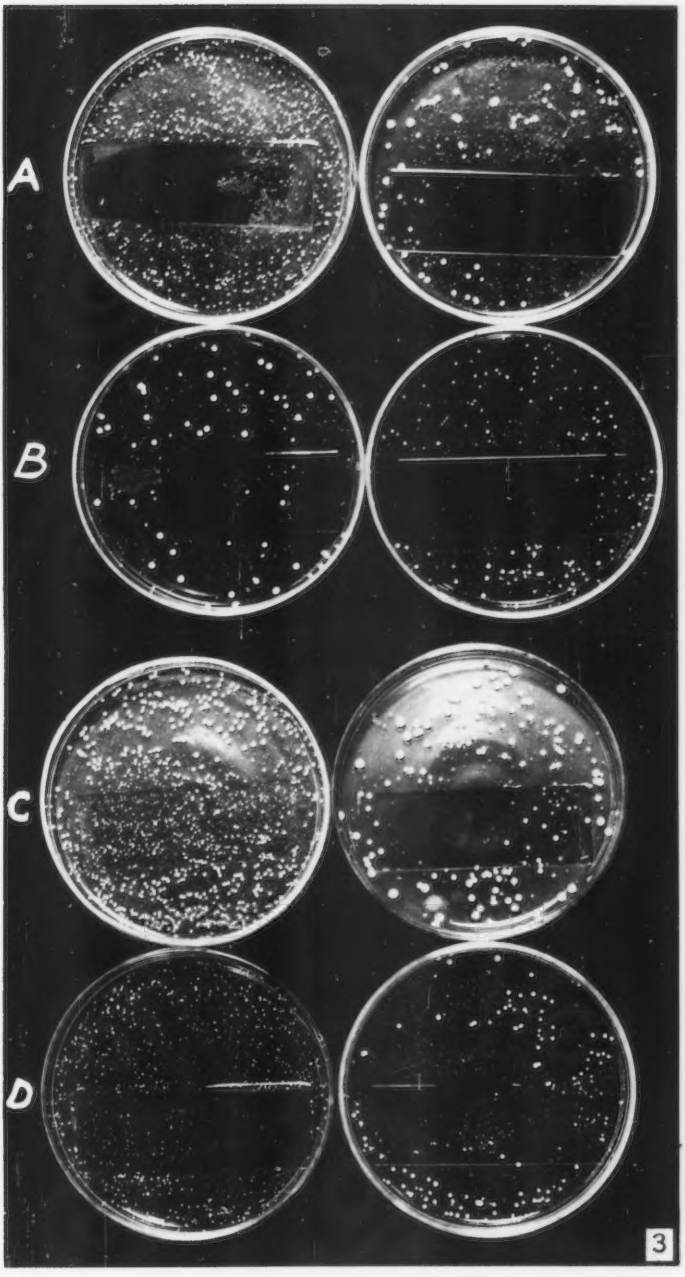
A
B
C
D
3

telling nothing about the proportion of the organisms surviving after shorter periods of exposure; (*b*) it measures the killing effect of germicides where the test organisms are freely suspended in the solution of germicide, rather than in a film on a surface; and (*c*) it is based upon the determination of the concentration of germicide required to give complete killing in 10 min., but not in 5, rather than the measurement of the effectiveness of the germicide in the concentrations used in practice (19, 26). It was largely to avoid these objections that the glass slide technique was devised. In this technique, the organisms are present in a partially dried film of skim-milk, thus simulating conditions encountered in the sanitizing of food handling utensils and equipment. The proportion of skim-milk is of course far in excess of that that would be encountered on well washed equipment, but occasionally slip-ups do occur, and it is well to have the test method cover the most extreme conditions likely to be encountered.

In addition to approximating more closely the conditions under which bacteria have to be destroyed in plant sanitizing procedures, the glass slide method has other advantages. It possesses great flexibility in that the temperature, period of exposure, test organism, plating medium, concentration of germicide, etc., may all be varied to suit the requirements of the investigator. As to reproducibility of results, far less variability can be expected than with tests of the phenol coefficient type. A final point is that through gentle agitation of the slide during the period of contact with the germicide, any superiority of detergent action of a given product has an opportunity to exert itself, and, by mechanical removal of the film and its accompanying bacteria, reduce the number of organisms remaining on the slide.

The bacteriostatic influence of the small quantity of quaternary compound carried over on the slide after rinsing in tap water is not believed to have influenced the comparisons between these products and hypochlorites significantly. While with strong solutions the effect is quite evident on a crowded plate, with the usual concentrations it is practically unnoticeable when the number of colonies approaches the 99.9% end-point. From a practical standpoint, this continuing effect may be regarded as an advantage, as sterilization of metal surfaces of utensils and equipment would continue for some time in the residual film of solution. In view of the findings of Valko and DuBois (35) and others, the failure of attempts to neutralize this bacteriostatic action by rinsing in solutions of anionic compounds was surprising. Possibly orientation of the adsorbed molecules of quaternary compounds leaves the actively germicidal groups in contact with the milk film, so that the anionic molecules cannot react with them.

These studies indicate that it is unsafe to generalize concerning the relative values of quaternary compounds and hypochlorites in the sanitizing of food plant equipment. Much depends upon the type of organism most likely to be prevalent. As was shown to be the case with chlorine sterilizing agents (19, 20), some quaternary products are more effective than others. An im-

portant point in plant operations is that hypochlorites respond much more readily to favourable adjustments of pH and temperature than do the quaternary compounds tested.

Despite their greater stability, non-corrosiveness and other desirable features, their higher cost makes it unlikely that quaternary compounds will immediately replace hypochlorites in most phases of plant sanitation. There are, however, certain special fields in which they may excel. One is in the sanitizing of egg breaking sets; the emollient effect of the quaternary solution contrasts with the irritating effect of hypochlorites on the skin, hence breakers or kitchen help are much less averse to putting their hands into the sanitizing solution when treating washed breaking sets. There is the further point that certain of these quaternary compounds leave on the hands a resistant invisible film that retains bacteria beneath it (27). Another is in the treatment of milk shipping cans; whether cans are washed by hand or by machine, a small percentage of a suitable quaternary compound in the final rinse would help prevent growth of bacteria in remaining traces of moisture, while reducing the corrosion that generally follows the use of the more active hypochlorites for such a purpose. Similarly, in the treatment of beverage glasses, dishes, and silverware, the quaternary compounds leave less odour and are easier on the skin, while their lower sensitivity to added organic matter maintains the germicidal potency longer than is the case with hypochlorites.

The greater effectiveness of the quaternary compounds against spores of *B. panis* is of interest in that Scales and Kemp (33) reported that Roccal was ineffective against spores of *B. subtilis*. On the other hand, Green and Birkeland (11) found cetylpyridinium chloride effective against spores of *B. subtilis* and other aerobic and anaerobic species, and Heineman (12) reported destruction of spores of *B. subtilis* in less than five minutes by 2,000 p.p.m. of Roccal. The ineffectiveness of the chlorine compounds is in line with previous findings (15).

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THE EFFECT OF WEATHERING ON VARIOUS ROTPROOFING TREATMENTS APPLIED TO COTTON TENTAGE DUCK[1]

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Abstract

Cotton tentage duck treated with ferric oxide–chromic oxide ('mineral khaki'), copper carbonate–ferric oxide ('copper–iron'), cuprammonium, cutch–cuprammonium, copper 8-quinolinate, copper glyoxime, 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane, zinc dimethyldithiocarbamate, copper naphthenate, copper hydroxynaphthenate, zinc naphthenate, and mercuric naphthenate, showed varying degrees of breaking strength loss when subjected to outdoor weathering during the summer months. The losses were in no case greater than that of the untreated fabric, and certain treatments, such as mineral khaki and cutch–cuprammonium, gave considerable protection against loss in breaking strength. With copper naphthenate, copper hydroxynaphthenate, and mercuric naphthenate the degree of chemical degradation as measured by cuprammonium fluidity was somewhat greater than that of the untreated fabric. The presence of a waterproofing treatment consisting of a mixture of petroleum-base waxes in addition to the rotproofing treatments usually resulted in increased breaking strength loss. The water resistance of the waxed samples showed a slight to pronounced increase on weathering. In general there was considerable loss of rotproofer as a result of weathering; with the copper compounds this loss was of the order of 37 to 90%, but was reduced to 6 to 44% by the presence of wax. Weathering produced an almost complete loss of the two zinc compounds, 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane, and mercuric naphthenate. Losses of metal from chromium–iron proofings were negligible even in the absence of wax proofing. The degree of rot resistance as judged by soil burial was greatest in the fabrics treated with copper, and was increased by the presence of wax. The water resistance of samples subjected to soil burial was frequently decreased before the occurrence of any marked loss in breaking strength; this indicates microbiological attack on the wax coating prior to attack on the cotton fabric.

The weathering characteristics of chemical substances used for the purpose of imparting resistance to microbiological attack in cotton textiles for outdoor use are of considerable importance. In addition to the obvious disadvantages of those compounds possessing an appreciable solubility in water or poor stability to sunlight, it is undesirable for the compound to catalyze the actinic degradation of the fabric.

It has been reported that impregnation of cotton fabrics with certain compounds such as chromic oxide (9, 10, 16) or certain copper–tannin complexes (1) results in increased resistance to actinic degradation. Hayes (13) states that the fastness to light and weather conditions of the chromic oxide–ferric oxide treatment known as 'mineral khaki' was not excelled by any other treatment. The action of waterproofing waxes on the chemical degradation of cotton yarns (14) and canvas (15) has been studied by Jarrell and Holman, who found that the presence of such waxes in cotton yarns subjected to weathering did not result in increased actinic degradation while with cotton duck, especially where 'yellow petrolatum' was used, there was a marked increase in the extent

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of degradation. Jarrell and Holman attribute these differences to the greater degree of heating to which the cotton duck was exposed during the weathering process. The degradation was markedly reduced by the inclusion of pigments with the wax. It has been shown that the presence of copper soaps used as rotproofers in concentrations up to 1% copper did not materially increase the extent of actinic breakdown occurring in cotton tarpaulin duck (4) and in various types of cordage fibres (3). It was also found (4) that the presence of a wax-pigment-filler type of compound in conjunction with the copper rotproofer resulted in decreased breaking strength and metal losses on weathering.

In the present study the weathering characteristics of a number of rotproofers applied to cotton tentage duck, with and without waterproofing wax, have been studied. The extent of the degradation produced by weathering was judged by the extent of breaking strength loss and increase in cuprammonium fluidity, while the loss in rotproofing efficacy was determined by means of the standard soil burial technique. Measurements of changes in water resistance and loss of rotproofer resulting from weathering were also carried out.

Materials Used

The fabric used was an unbleached cotton army duck weighing 10 oz. per sq. yd. and having 46 three-ply yarns per inch in the warp and 37 two-ply yarns per inch in the weft. With the exception of the 8-hydroxyquinoline and dimethylglyoxime, all the chemicals used were of technical (commercial) grade.

Details of Treatments

The concentrations of treating compounds applied to the fabric were chosen on the basis of previous experience or of recommendations received from other investigators. With few exceptions, as indicated, the treatments were applied in the laboratory, mostly by aqueous procedures. With copper, zinc, and mercuric naphthenates, the treatments were applied from solution in Stoddard solvent (dry cleaners' naphtha) as previously described (2). The copper naphthenate treated fabric was of a pale blue-green colour, the others colourless.

A number of 12 in. (warpwise) by 18 in. (weftwise) specimens were cut from a single bolt of fabric and, of these, four were selected at random for each treatment. Two of these specimens were subjected to weathering, the other two being tested as indicated below without previous weathering. The two weathered specimens were each subdivided into four subspecimens, each of which was sufficient to provide five 1-in. wide ravelled warp strips for breaking strength determinations. Breaking strength determinations were run on the first subspecimen from each of the two weathered specimens (two replicates of five breaks each), on the second pair of subspecimens after burial for two weeks, on the third after burial for four weeks, the fourth subspecimen being held in reserve. The two unweathered specimens were also divided

into four subspecimens as above, and breaking strength determinations carried out on the first subspecimen from each of the two specimens after leaching (original breaking strength), on the second pair of subspecimens after burial for two weeks without leaching, on the third after leaching and burial for two weeks, and on the fourth after leaching and burial for four weeks.

In the aqueous treatments the four 12 in. by 18 in. specimens for each treatment were sewn together along the 12 in. edge to form a strip, passed through the motor-driven rubber-covered rolls of a laboratory padder, which could be operated at a speed of 20 ft. per min., and the free ends of the strip connected through a 'runner' of fabric to form a continuous loop approximately 6 ft. in circumference. The runner was passed beneath a brass roll and the latter lowered into the treating solution (10 litres) contained in an enamelled pan that could be heated when necessary, and the loop of fabric run through the bath. At the conclusion of the treatment, unless otherwise indicated, the fabric was washed for two hours in running tap water and dried at room temperature. In all the aqueous treatments the loop of fabric was previously wetted out by passage through a solution of a wetting agent (a 0.1% solution of technical sodium lauryl sulphate in the form of Gardinol WA was used).

A duplicate series of treated samples was also prepared containing a waterproofing wax coating consisting of a mixture of paraffin wax* and petrolatum No. 2** having the following characteristics:

——	Parowax	Petrolatum No. 2
Melting point, ASTM, °F.	122 – 125	114 – 120
Say. visc. at 210° F., sec.	33 – 38	64 – 71
Penetration at 77° F., cone	—	170 – 220
Colour	+25+ Say. (water white)	35Y 70R 2 in. cell
Oil content, %	0.5 max.	About 35

The paraffin wax and petrolatum were used in a ratio of 3 : 1 by weight, and were applied subsequent to the rotproofing treatment from a Stoddard solvent bath having a concentration calculated to give approximately 10% of wax on the weight of the fabric. When the rotproofer was applied from solution in Stoddard solvent, the wax was incorporated in the solution containing the rotproofer.

The details of the aqueous treatments are given below. The weight of chemicals shown refers to the amount added to 10 litres of distilled water; the temperatures of the treatments and the length of time during which the loop of fabric was run through the treating bath are also shown.

* *'Parowax' (refined paraffin wax), Imperial Oil Ltd.*
** *'Petrolatum No. 2' Imperial Oil Co.*

(1) Chromium–iron ('Mineral Khaki')

Bath (1)—1200 gm. chromic sulphate ($Cr_2(SO_4)_3 . 5H_2O$) plus 500 gm. ferrous sulphate at 70° C. for 15 min.

Bath (2)—500 gm. sodium hydroxide at room temperature for 30 sec.

Colour of treated fabric—medium tan.

In addition to the sample treated as above, a sample of commercially processed chromium–iron ('mineral khaki') proofed tentage duck* was included in this series. In view of the fact that chromium–iron treated fabrics are known to show poor rot resistance when exposed to conditions of heavy contamination, e.g., soil contact, it was thought desirable to investigate the characteristics of a chromium–iron sample aftertreated with copper naphthenate, a substance that is known to have good resistance to possible deterioration resulting from soil contact. Samples of the commercially processed fabric were therefore treated with copper naphthenate applied from a solvent bath as previously described (2).

(2) Copper–iron

This treatment, involving the impregnation of the fabric with a mixture of copper and iron salts followed by passage through a solution of sodium carbonate, is based on the finding of Race and co-workers at the University of Leeds (19). The concentrations of the treating solutions were adjusted to give metal contents on the treated fabric of 0.5 to 1.0% copper oxide and 0.7 to 1.25% ferric oxide.

Bath (1)—930 gm. ferric ammonium sulphate ($Fe_2(SO_4)_3(NH_4)_2SO_4 . 24H_2O$) plus 990 gm. copper sulphate ($CuSO_4 . 5H_2O$) at 70° C. for 15 min.

Bath (2)—500 gm. sodium carbonate (anhydrous) at 50° C. for 10 min.

Colour of treated fabric—orange tan.

(3) Cutch–cuprammonium

The cutch (quebracho) extract used in this treatment was in solid form.

Bath (1)—200 gm. cutch dispersed in 5 litres of water and added to 100 gm. of copper sulphate dissolved in 5 litres of water; run at 70° C. for 20 min.

Bath (2)—100 gm. sodium dichromate at 50° C. for 15 min.

Bath (3)—500 gm. copper sulphate, dissolved in water and ammonium hydroxide added until the precipitate was just dissolved; run at room temperature for 15 min.

Colour of treated fabric—chocolate brown.

(4) Copper Hydroxynaphthenate

A stock solution of 200 gm. Nuodite Copper 25%† in 250 gm. ammonium hydroxide (28% NH_3) was diluted with water to give the desired copper

* *Obtained from the Chief Inspector of Stores, Central Ordnance Depot, Didcot, Berks., England.*

† *Obtained from Nuodex Products of Canada Ltd., Leaside (Toronto), Ont.*

content on the fabric, and the fabric run through the solution for 20 min. at room temperature.

Colour of treated fabric—a pale blue-green somewhat lighter than that of copper naphthenate.

(5) Copper 8-Quinolinate

This treatment was based on recommendations received from the Monsanto Chemical Co. (12).

Bath (1)—625 gm. glacial acetic acid mixed with 312 gm. 8-hydroxyquinoline and the mixture added to 10 litres of water. Run at 82° to 88° C. for 15 min.

Bath (2)—200 gm. copper acetate ($Cu(C_2H_3O_2)_2H_2O$) at room temperature for 10 min.

Colour of treated fabric—greenish yellow.

(6) Copper Glyoxime

The procedure was a modification of the method of Neish and co-workers (17).

Bath (1)—100 gm. dimethylglyoxime at 98° C. for 10 min.

Bath (2)—100 gm. copper acetate at room temperature for 30 min.

Colour of treated fabric—yellow green.

(7) 2,2'-Dihydroxy-5,5'-dichlorodiphenylmethane

A commercial preparation of this compound in the form of the product G-4* was applied from solution in sodium hydroxide and the free base precipitated in the fabric by treatment with acetic acid.

Bath (1)—160 gm. G-4 and 28.8 gm. sodium hydroxide at room temperature for 15 min.

Bath (2)—500 gm. glacial acetic acid at room temperature for 15 min. For the treatment at the lower concentration, Bath (1) was diluted 1 : 1 with distilled water. Owing to the alkalinity of the Ottawa tap water the rinsing of the treated fabric was carried out in distilled water.

Colour of treated fabric—unchanged.

(8) Zinc Dimethyldithiocarbamate

In applying this treatment the fabric was impregnated with a solution of commercial sodium dimethyldithiocarbamate** and the zinc compound precipitated by passage through a solution of zinc sulphate.

Bath (1)—200 gm. sodium dimethyldithiocarbamate solution (stated by the manufacturer to have a nitrogen content of 3.29% corresponding to approximately 30% active ingredient) at room temperature for 15 min.

* *Obtained from Givaudan Delawanna Inc., 330 W. 42nd Street, New York.*

** *Obtained from Naugatuck Chemicals, Elmira, Ont.*

Bath (2)—100 gm. zinc sulphate at room temperature for 10 min.
For the treatment at lower concentration, Bath (1) was diluted 1 : 1 with distilled water.

Colour of treated fabric—unchanged.

(9) Cuprammonium

This was a commercially proofed sample*, medium green in colour.

Methods

The fabrics were weathered on the eastern end of the roof of the National Research Laboratories, Sussex Street, Ottawa, from May 31, 1945, to Sept. 30, 1945. The samples were fixed to wooden racks that were set at an angle of 45° facing southwest, care being taken on the one hand to avoid attaching the samples to the frames under tension, and on the other to avoid a degree of looseness such as would permit undue flapping of the samples in the wind. The distance from the roof to the lower edge of the samples was 2½ ft. A record of maximum and minimum temperatures during the exposure period was kept by means of a thermometer attached to one of the racks.

Rot resistance was determined by the soil burial method (7), tests being run on the original, weathered, and leached samples. Leaching was carried out in 1 litre bottles through which tap water at 25° C. flowed at a rate of 10 litres per hour, the duration of leaching being 24 hr. Breaking strength measurements were made by the ravelled strip method on specimens ravelled to 1 in. and conditioned at 70° ± 5° F. and 65% relative humidity ± 2%. Water resistance was measured by the variable head method (6). Cuprammonium fluidity measurements were carried out on conditioned samples using the method of Clibbens and Little (8). The portions of the waxed samples used for fluidity determinations were previously freed of wax by extraction with Stoddard solvent. Copper analyses were made by the ignition method (5). The preliminary phases of the chromium and iron determinations were made by Method 35 C of the analytical methods recommended by the Textile Institute of Great Britain (21), the chromium determinations being completed by Method 37 (*a*) and the iron determinations by the method of Race (18). In the latter method the iron in the hydrochloric acid solution was reduced by the addition of a few drops of stannous chloride solution (3% solution in 3 *N* hydrochloric acid). The solution was cooled, 2 ml. saturated mercuric chloride solution was added to destroy excess stannous chloride, and the solution titrated immediately with *N*/10 potassium dichromate using barium diphenylamine *p*-sulphonate as indicator. Copper and iron when present together were determined by the method of Race (18) with a slight modification of the procedure for copper—i.e., to the ammoniacal filtrate acetic acid was added in slight excess and the solution titrated with thiosulphate as in the method for copper alone (5).

* *Obtained from the Willesden Proofing Co. Inc., New York, N.Y., U.S.A.*

Zinc in fabrics treated with zinc naphthenate was determined by the hydrolysis method (26), the acid solution being titrated with ferrous ammonium sulphate (25). Zinc dimethyldithiocarbamate was determined by the colorimetric method (22) involving conversion to the copper compound, mercury by the method of Shiraeff (20), and 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane by the method of Gottlieb and Marsh (11). Determinations of the pH of the untreated fabric were made according to the method of Wakeham and Skau (24).

Data

(1) Weather Conditions

From the weather data in Table I it will be noted that conditions were favourable to actinic degradation. Comparison of weather conditions with those of the previous summer (4) shows that the average total hours of sunshine per month were similar but that the rainfall in the present series was markedly greater (4.19 in. per month compared with 2.57 in.). There was some evidence of superficial growth of a species of the fungus *Alternaria* on the underside of the untreated fabric.

TABLE I

WEATHER CONDITIONS DURING EXPOSURE OF SAMPLES

Period	Mean daily temperature, °F.		Rainfall, in.	Bright sunshine, total hours
	Maximum	Minimum		
May 31 – June 3	56	37	0	35.9
June 4 – June 10	66	43	1.00	52.0
June 11 – June 17	82	59	1.17	48.7
June 18 – June 24	79	57	0.32	55.3
June 25 – July 1	90	59	0.64	67.7
July 2 – July 8	86	62	0.10	76.4
July 9 – July 15	78	56	2.29	38.1
July 16 – July 22	82	58	0.21	63.3
July 23 – July 29	90	66	0.13	64.3
July 30 – Aug. 5	89	61	1.10	59.6
Aug. 6 – Aug. 12	93	58	0.47	57.3
Aug. 13 – Aug. 19	87	59	0.50	54.6
Aug. 20 – Aug. 26	89	56	1.91	51.2
Aug. 27 – Sept. 2	82	58	1.13	40.8
Sept. 3 – Sept. 9	94	64	0.07	58.5
Sept. 10 – Sept. 16	84	56	0.79	39.2
Sept. 17 – Sept. 23	62	45	3.20	28.4
Sept. 24 – Sept. 30	68	47	1.73	29.0
Average	81	56		
Total			16.76	920.3

(2) Breaking Strength Loss

Breaking strength data are given in Table II. The breaking strength losses of treatments that were applied to fabric cut from the same bolt were subjected to statistical analysis. It became apparent that the effects of the various treatments were significantly different in both the waxed and unwaxed samples

TABLE II

EFFECT OF WEATHERING AND BURIAL ON LOSS OF BREAKING STRENGTH

Treatment	Original breaking strength, lb.	Breaking strength loss, %					
		Weathered	Buried 2 weeks	Leached buried 2 weeks	Weathered buried 2 weeks	Leached buried 4 weeks	Weathered buried 4 weeks
Not waxed							
Untreated	175	41.7	97.8	100.0	89.0	100.0	100.0
Chromium–iron	163	8.6	88.4	94.5	90.8	100.0	100.0
*Chromium–iron	150	22.0	64.0	83.3	93.3	100.0	—
*Chromium–iron aftertreated with copper naphthenate	152	11.2	Zero	11.2	20.4	24.3	—
Copper–iron	204	45.6	4.9	2.5	55.7	8.8	94.5
*Cuprammonium	139	38.9	+7.2	+11.5	50.0	+18.0	54.8
Cutch–cuprammonium	175	17.7	5.2	2.9	38.2	1.7	25.6
Copper naphthenate	174	40.3	4.0	12.6	64.4	39.1	100.0
Copper hydroxynaphthenate	161	33.0	+4.4	0.6	62.1	57.8	100.0
Copper 8-quinolinate	197	33.0	+0.5	1.0	43.3	23.4	47.3
Copper glyoxime	162	27.2	+9.9	6.8	47.6	1.2	88.9
Zinc dimethyldithiocarbamate (*A*)	169	43.8	+3.0	12.4	86.3	93.0	100.0
Zinc dimethyldithiocarbamate (*B*)	161	37.2	+4.4	+7.5	86.3	34.2	100.0
Zinc naphthenate	177	38.4	19.8	27.1	82.7	92.7	100.0
Mercury naphthenate	158	41.2	100.0	100.0	78.5	100.0	100.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*A*)	157	38.2	+10.2	67.5	83.4	100.0	100.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*B*)	164	45.1	+9.7	56.7	71.9	100.0	100.0
Waxed							
Untreated	188	70.8	99.5	96.9	88.2	100.0	—
Chromium–iron	191	34.5	67.5	62.9	82.1	100.0	100.0
*Chromium–iron	163	28.2	25.2	23.9	57.0	100.0	100.0
*Chromium–iron aftertreated with copper naphthenate	163	22.1	1.2	3.7	23.9	7.4	41.7
Copper–iron	193	36.8	5.7	20.2	38.0	14.0	41.0
*Cuprammonium	167	62.4	+3.6	0.6	56.4	0.6	61.5
Cutch–cuprammonium	191	27.2	+0.5	1.5	31.1	14.7	31.1
Copper naphthenate	184	57.1	9.8	5.4	62.5	13.6	59.2
Copper hydroxynaphthenate	189	55.0	16.4	16.4	57.2	41.8	58.3
Copper 8-quinolinate	192	30.7	2.1	1.0	34.9	6.3	34.9
Copper glyoxime	192	53.2	21.4	16.7	54.7	24.5	57.2
Zinc dimethyldithiocarbamate (*A*)	196	66.9	17.9	19.9	85.7	91.4	100.0
Zinc dimethyldithiocarbamate (*B*)	194	67.5	17.0	21.6	79.8	46.4	100.0
Zinc naphthenate	187	69.5	11.2	19.8	82.9	82.4	100.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*A*)	184	65.8	3.3	28.2	79.3	82.6	100.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*B*)	185	68.6	+8.1	0.5	75.1	15.1	100.0

* *Commercially treated.*

under all conditions of weathering and burial. The necessary difference between sample averages of breaking strength loss (10 breaks) for significance at the 5% level is approximately 12% for all treatments involving soil burial, and approximately 6% for those involving weathering.

(a) Weathering Effects

The colour of the chromium–iron treated fabric was not changed by weathering, all of the other coloured fabrics unwaxed showing some fading. The copper–iron and cutch–cuprammonium treatments retained considerable brown coloration but the upper surface of the other copper treated fabrics was colourless.

The untreated fabric showed a substantial breaking strength loss and this was more pronounced in the presence of wax. The unwaxed samples treated with chromium–iron, cutch–cuprammonium, copper hydroxynaphthenate, copper 8-quinolinate, and copper glyoxime treatments showed lower breaking strength losses than the untreated fabric. The waxed samples, with the same treatments and, in addition, copper–iron, cuprammonium, and copper naphthenate, were superior to the waxed untreated sample. In general the breaking strength losses of the waxed samples were greater than those of the unwaxed, the only exceptions being the commercial chromium–iron, copper–iron, and copper 8-quinolinate treated samples. With the unwaxed and waxed commercially treated chromium–iron samples aftertreated with copper naphthenate, it will be noted that the presence of the copper naphthenate did not increase the breaking strength loss above that shown by the samples containing chromium–iron alone.

(b) Burial Effects

Unwaxed treatments that were completely resistant to soil burial for four weeks with preliminary leaching were the copper–iron, cuprammonium, cutch–cuprammonium, and copper glyoxime. Treatments that withstood burial for two weeks but gave moderate losses after four weeks were chromium–iron + copper naphthenate, copper naphthenate, copper hydroxynaphthenate, copper 8-quinolinate, and zinc dimethyldithiocarbamate (0.49%). 2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane was resistant to burial for two weeks without leaching, but with preliminary leaching the breaking strength losses were substantially increased. Zinc naphthenate suffered moderate breakdown on two-week burial and almost complete breakdown after four weeks. The chromium–iron and mercury naphthenate treated fabrics showed little resistance to soil burial but the commercial chromium–iron fabric aftertreated with copper naphthenate was resistant. The addition of wax frequently caused a substantial reduction in the breaking strength loss as for example in samples containing 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane when leached and buried for two and four weeks.

The losses in breaking strength of all samples subjected to soil burial after weathering were substantial although when allowance is made for the losses produced by weathering alone the effect attributable to soil burial is not excessive in most cases. Thus in the unwaxed fabrics, burial for four weeks after weathering produced no additional loss in strength with the cutch–cuprammonium, and barely significant losses with the cuprammonium and copper 8-quinolinate treated samples. All other unwaxed treated samples

showed almost complete breakdown when buried for four weeks after weathering, although burial for two weeks after weathering produced no loss in strength additional to that shown on weathering alone with the chromium–iron treatment with a copper naphthenate aftertreatment and copper–iron treated samples, and caused only 20 to 30% loss in strength in the copper glyoxime, copper naphthenate, and copper hydroxynaphthenate treated samples. In the case of the unwaxed samples, with the exception of the chromium–iron aftertreated with copper naphthenate, none of the copper treatments showed significant increases in breaking strength loss as a result of four weeks' burial after weathering, all the other waxed treatments showing complete breakdown.

(3) Loss of Treating Compound

Data for the loss of the treating compounds as a result of weathering are given in Table III. With the treatments containing chromium and iron, it had

TABLE III

LOSS OF TREATING COMPOUND ON WEATHERING

Treatment	Analysis	Not waxed			Waxed		
		Concentration, %		Loss on weathering, % of orig.	Concentration, %		Loss on weathering, % of orig.
		Orig.	Weath.		Orig.	Weath.	
Chromium–iron	Cr	1.28	1.26	1.5	1.14	1.20	+ 5.3
	Fe	0.70	0.60	14.3	0.60	0.68	+13.3
*Chromium–iron	Cr	0.80	0.85	+ 6.2	0.75	0.85	+13.3
	Fe	0.77	0.64	18.6	0.76	0.58	23.7
*Chromium–iron aftertreated with copper naphthenate	Cr	0.75	0.79	+ 5.3	0.82	0.77	6.1
	Fe	0.77	0.70	9.1	0.76	0.78	+ 2.6
	Cu	0.19	0.12	36.8	0.16	0.14	12.5
Copper–iron	Cu	0.65	0.07	89.1	0.50	0.54	+ 8.0
	Fe	0.70	0.66	5.7	0.70	0.78	+11.4
*Cuprammonium	Cu	1.41	0.72	49.0	1.40	1.11	20.7
Cutch–cuprammonium	Cu	1.85	0.53	71.5	1.46	1.21	17.1
Copper naphthenate	Cu	0.33	0.08	75.7	0.31	0.18	41.9
Copper hydroxynaphthenate	Cu	0.34	0.07	70.6	0.34	0.22	35.3
Copper 8-quinolinate	Cu	0.80	0.15	81.3	0.72	0.68	5.6
Copper glyoxime	Cu	0.49	0.10	79.6	0.48	0.27	43.8
Zinc dimethyldithiocarbamate (*A*)	Total compound	0.29	0.00	100.0	0.20	0.02	90.0
Zinc dimethyldithiocarbamate (*B*)	Total compound	0.49	0.04	91.9	0.45	0.05	88.8
Zinc naphthenate	Zn	0.79	0.00	100.0	0.88	0.00	100.0
Mercury naphthenate	Hg	0.01	0.00	100.0	—	—	—
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*A*)	Total compound	0.55	0.02	96.3	0.48	0.01	98.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*B*)	Total compound	1.00	0.13	87.0	0.91	0.07	91.2

* *Commercially treated.*

been noted that the distribution of these elements in the treated fabric was not as uniform as would have been expected, and this undoubtedly accounts for the apparent increase in the content of these elements noted in some of the weathered samples. The data are sufficient to indicate that there is no substantial loss of either chromium or iron during weathering. The copper concentration of all copper treatments was reduced substantially by weathering. In the unwaxed treatments there was less copper lost from the chromium–iron aftertreated with copper naphthenate treatment than from any of the other copper treatments. This effect is being studied further. The presence of wax reduced the loss of copper, there being practically no loss from the waxed copper–iron and copper 8-quinolinate treatments, and only moderate losses with the other copper treatments. In the latter group the percentage loss of copper from the cuprammonium and cutch–cuprammonium treatments was lower than that from copper naphthenate, copper hydroxynaphthenate, and copper glyoxime. It should, however, be borne in mind that these original concentrations of copper in the cuprammonium and cutch–cuprammonium treatments were higher than in the other copper treatments. The other treating compounds, namely zinc dimethyldithiocarbamate, zinc naphthenate, mercury naphthenate, and 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane were removed either completely or almost completely by weathering.

(4) Water Resistance

Comparison of the laboratory samples to which wax was applied from a solution in Stoddard solvent in a separate operation after the rotproofing treatment shows that the original water resistance of the treated fabrics was somewhat higher than that of the untreated fabric containing wax alone (Table IV), although, on weathering, the water resistance of the untreated waxed sample was increased. For all treatments except the chromium–iron, in which the water resistance decreased slightly on weathering, the water resistance was increased on weathering. For samples that had been leached and buried for four weeks the water resistance of the cuprammonium, copper 8-quinolinate, and 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane (0.91%) was approximately the same as, or greater than, the original value, the resistance of the other treatments being substantially reduced.

(5) Cuprammonium Fluidity

The cuprammonium fluidity data are given in Table V. It is apparent that the fluidity of the original cutch-cuprammonium treated fabric is slightly higher than that of the untreated fabric. In all other laboratory treatments there is no evidence of chemical damage resulting from the treating procedures. Although it was not possible to measure the fluidity of the untreated fabric from which the commercially treated chromium–iron sample had been prepared, the fluidity of the commercial chromium–iron samples appears considerably higher than that usually obtained with an unbleached cotton duck, and it is therefore reasonable to conclude that some chemical damage had occurred in the commercial processing of this sample. On weathering,

TABLE IV

EFFECT OF WEATHERING AND BURIAL ON WATER RESISTANCE OF WAXED FABRICS

Treatment	Water resistance, cm. pressure to cause leakage			Change in water resistance, % of original	
	Orig.	Weath.	Leached and buried four weeks	Weathered	Leached and buried four weeks
Untreated	29	44	0	+52	−100
Chromium–iron	55	51	0	− 7	−100
*Chromium–iron	35	—	0	—	−100
*Chromium–iron aftertreated with copper naphthenate	38	33	19	−13	− 50
Copper–iron	45	53	20	+18	− 56
*Cuprammonium	40	49	54	+23	+ 35
Cutch–cuprammonium	50	55	17	+10	− 66
Copper naphthenate	32	47	21	+47	− 34
Copper hydroxynaphthenate	47	51	18	+ 9	− 62
Copper 8-quinolinate	50	55	52	+10	+ 4
Copper glyoxime	44	49	12	+11	− 73
Zinc dimethyldithiocarbamate (*A*)	39	47	9	+21	− 77
Zinc dimethyldithiocarbamate (*B*)	40	44	—	+10	—
Zinc naphthenate	27	41	13	+52	− 52
2,2′-Dihydroxy-5,5′-dichloro-diphenylmethane (*A*)	35	54	14	+54	− 60
2,2′-Dihydroxy-5,5′-dichloro-diphenylmethane (*B*)	35	52	40	+49	+ 14

* *Commercially treated.*

the untreated fabric showed a considerable increase in fluidity, the effect being slightly more pronounced in the waxed fabric. With the unwaxed samples the rise in fluidity was markedly less than that of the untreated fabric for the chromium–iron and copper 8-quinolinate treatments. With the waxed samples the copper–iron, cutch–cuprammonium, and copper glyoxime treatments were also effective in reducing chemical degradation. Copper naphthenate, with and without wax, and copper hydroxynaphthenate and mercury naphthenate, unwaxed, showed increases in cuprammonium fluidity somewhat greater than that shown by the untreated fabric.

Discussion of Data

Attention is called to the appreciable amount of degradation on weathering which took place in the waxed samples as compared with the unwaxed samples. It was thought that the wax coating might have caused the adherence to the fabric of particles of acidic dirt from the air, and consequently a comparison of the pH of the waxed and unwaxed fabrics after weathering might be of value (Table VI). It will be noted that the pH values for waxed and unwaxed fabrics are similar and, although the decrease in pH value as the result of

TABLE V

EFFECT OF WEATHERING ON CUPRAMMONIUM FLUIDITY

Treatment	Cuprammonium fluidity, reciprocal poises					
	Not waxed			Waxed		
	Orig.	Weath.	Increase on weathering	Orig.	Weath.	Increase on weathering
Untreated	3.3	16.8	13.5	3.9	20.6	16.7
Chromium–iron	3.1	7.3	4.2	3.2	6.1	2.9
*Chromium–iron	8.3	16.6	8.3	7.2	15.5	8.3
*Chromium–iron aftertreated with copper naphthenate	9.9	14.2	4.3	9.5	15.0	5.5
Copper–iron	2.8	14.7	11.9	4.0	8.0	4.0
*Cuprammonium	4.5	17.2	12.7	4.7	18.0	13.3
Cutch–cuprammonium	5.8	19.1	13.3	5.9	16.7	10.8
Copper naphthenate	2.5	21.7	19.2	2.4	21.7	19.3
Copper hydroxynaphthenate	2.7	20.6	17.9	3.1	18.4	15.3
Copper 8-quinolinate	2.4	12.3	9.9	3.3	10.8	7.5
Copper glyoxime	2.4	17.3	14.9	3.3	12.6	9.3
Zinc dimethyldithiocarbamate (*A*)	2.5	16.3	13.8	3.9	20.7	16.8
Zinc dimethyldithiocarbamate (*B*)	2.5	14.4	11.9	3.3	19.8	16.5
Zinc naphthenate	3.0	17.0	14.0	3.3	19.9	16.6
Mercury naphthenate	2.8	21.1	18.3	—	—	—
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*A*)	2.8	15.2	12.4	3.7	19.7	16.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*B*)	2.8	15.7	12.9	2.2	19.6	17.4

* *Commercially treated.*

TABLE VI

pH OF UNTREATED FABRIC

Sample	pH	
	Original	Weathered
Untreated, not waxed	6.2	5.9
Untreated, waxed	6.7	5.6

weathering is greatest for the waxed fabric, it is not considered that the final value for the pH of the latter fabric is indicative of the possibility of damage through acid attack. The damage must therefore be attributed to oxidative changes intensified by the presence of the wax compound, and this effect is being studied further.* Mention has already been made of the findings of Jarrell and Holman (15) with regard to the deteriorating effect of yellow

* *Indications are that the increased degradation is attributable to a great extent, if not entirely, to the petrolatum.*

petrolatum on cotton canvas. These authors found that the addition of pigments decreased the deteriorating effect. It is therefore possible that in previous work in this laboratory on the weathering of cotton duck (4) the inclusion of iron oxide pigment in the wax compound prevented any accelerated damage that might have been caused by the wax.

In general the breaking strength losses on burial of the waxed samples were less than those of the unwaxed and also the loss of treating compound on weathering was less marked. However, in the waxed samples treated with zinc dimethyldithiocarbamate, zinc naphthenate, and 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane the treating compound was almost completely removed on weathering, so that the behaviour with respect to soil burial after weathering was similar to that of the untreated fabric. It might be mentioned that the untreated fabric that had been weathered was slightly superior on burial to the original untreated fabric. This factor is in agreement with other observations that weathering retards subsequent attack by microorganisms (2, 4, 10, 16, 23).

With regard to the water resistance of the waxed fabrics after burial it may be noted that the treatments that showed no change in water resistance, namely cuprammonium, copper 8-quinolinate and 2-2′-dihydroxy-5,5′-dichlorodiphenylmethane (0.91%) also showed no appreciable change in breaking strength when leached and buried for four weeks. Fabrics containing other treatments that gave either no loss or slight loss in breaking strength when leached and buried for four weeks, namely chromium–iron aftertreated with copper naphthenate, copper–iron, cutch–cuprammonium, and copper naphthenate, showed substantial loss of water resistance. This would indicate that the water resistance is destroyed through microbiological attack on the wax before destruction of the cellulose takes place.

The data give additional evidence of the beneficial effect of the chromium–iron treatment in protecting against photochemical degradation, but also of the inability of this treatment to withstand exposure to conditions of severe contamination such as exist in the soil burial test. The addition of copper naphthenate to chromium–iron improved the rot resistance without affecting the resistance of the treated fabric to weathering. Race and Rowe (18) have reported that the addition of copper to chromium greatly diminishes or entirely destroys the protective value of chromium against weathering. The present data do not substantiate their findings. However, it should be pointed out that in their experiments the chromium oxide content was quite low, 0.39%, and also that the copper was in the form of the carbonate.

All copper compounds, without wax, showed considerable resistance to burial for two weeks even after preliminary weathering that had resulted in the removal of a large percentage of the copper. The cuprammonium, cutch–cuprammonium, and copper 8-quinolinate treatments were more satisfactory than the copper naphthenate, copper hydroxynaphthenate, and copper glyoxime, although it should be remembered that the copper concentrations of the former treatments were considerably higher than those of the latter

before and after weathering. With wax, the copper compounds all gave good resistance to burial for four weeks even after weathering.

It should be noted that from breaking strength data there was no evidence of enhanced photochemical degradation in the copper treated samples; in fact, the cutch–cuprammonium treatment with a copper concentration of 1.85% gave considerable protection, especially with the unwaxed sample. It is possible that the dark brown colour produced by this treatment had an effect in decreasing the photochemical degradation.

The Problem of the Protection of Tentage Ducks

One of the reasons for undertaking the present investigation was to obtain information regarding the weathering characteristics of a number of the more promising rotproofing treatments such as may be applicable to cotton duck used in the manufacture of tentage for the Canadian Armed Services.

The climatic conditions under which tentage may be used will vary widely, and several types of environments can be listed (Table VII).

TABLE VII

CONDITIONS OF VARIOUS ENVIRONMENTS IN WHICH MICROBIOLOGICAL ATTACK IS POSSIBLE

Environment number	Climatic zone	Season	Temperature	Rainfall	Sunlight intensity	Probable intensity of microbiological attack*
1	Temperate (open country)	Summer	Moderate to high	Moderate	High	Low to moderate
2	Temperate (varying degrees of shade)	Summer	Moderate	Moderate	Moderate to high	Low to moderate
3	Tropics (open country)	All seasons	Moderate to high	Moderate to high	High	Moderate
4	Tropics (shade–jungle)	All seasons	Moderate to high	Moderate to high	Low to moderate	High

** This refers to microbiological attack occurring in fabrics above ground level; under conditions of soil contamination, attack may be expected in all of the four environments.*

In addition to the environments given in Table VII reference should be made to the possibility of the occurrence of microbiological attack under conditions of storage. Experience has shown that cotton textiles in the temperate zone can readily undergo severe attack under conditions of humid storage at moderate to high temperatures in the spring, summer, and autumn seasons. Thus there are on record numerous cases in Canada of severe deterioration of untreated cotton textiles used in conjunction with service equipment (e.g., covers for army vehicles).

From a consideration of Table VII, it is reasonable to assume that provision should be made for the rotproofing of cotton tentage fabrics designed for use in environments Nos. 1 to 4, and, if such fabrics are liable to be used in *any* of these environments, the treatment chosen should be the one that provides the best resistance to microbiological attack and at the same time possesses good weathering characteristics with the minimum tendency to promote actinic degradation.

It has been shown in the present paper that the resistance to weathering of most of the rotproofers examined was markedly improved by a waxing treatment, but that the extent of actinic degradation is liable to be increased by the presence of wax. Moreover, it is sometimes argued that the loss in air permeability that results from waxing a tentage fabric is undesirable. For this reason there has been considerable interest in the range of so-called 'self-sealing' cotton canvases, recently developed by the British Cotton Industries Research Association, in which a high degree of water resistance, together with a normal level of air permeability, is obtained by a suitable choice of yarn twist factors and weaving densities. Hence, consideration may well be given to rotproofing treatments suitable for use on (*a*) ordinary tentage duck in which wax is used to increase the water resistance of the fabric, and (*b*) special ducks of the self-sealing type in which no wax treatment for the purpose of imparting water resistance is necessary.

In so far as requirement (*a*) is concerned, it is probable that a chromium–iron treatment aftertreated with copper naphthenate and wax, copper–iron waxed and copper 8-quinolinate waxed would be the most satisfactory. These treatments appear to exert a marked protective action against actinic degradation of the cotton while providing a high level of resistance to microbiological attack under conditions of severe contamination; the wax in such treatments provides a satisfactory level of water resistance and does not appear to enhance appreciably the actinic breakdown of the fabric. The losses of copper shown by these treatments on weathering were lower than those of any of the other copper compounds at the concentrations examined.

With respect to requirement (*b*) it is probable that the chromium–iron treatment aftertreated with approximately 3% copper naphthenate would be the most satisfactory. This treatment possesses all of the advantages cited for the three above-mentioned compounds except for the fact that the copper is removed to a marked degree by weathering. However, there should be no great difficulty in reapplying copper naphthenate to tentage in use. The copper–iron and copper 8-quinolinate treatments both showed severe loss of copper on weathering, and this loss could not be conveniently restored by re-treating in the field.

From time to time, objections have been raised to the use of copper naphthenate because of its characteristic odour. The odour of this compound varies between wide limits and it is believed that by the adequate specification of the properties of the naphthenic acids from which the compound is prepared, it should be possible to overcome this difficulty. The copper

naphthenates used in this laboratory have not possessed highly objectionable odours, and when applied to fabrics in the concentrations used in the various investigations on rotproofing have imparted little or no odour to the treated fabric.

Some mention might be made of the suitability of a chromium–iron treatment alone for use under requirements (*a*) and (*b*). This treatment, in which the chromium is the constituent toxic to micro-organisms, has long been widely used in Great Britain and, provided not less than 0.75% of chromium (as Cr_2O_3) is present, is known to possess a moderate degree of rotproofing efficacy. This treatment would probably be adequate for exposures above ground level, under the conditions of environment No. 1. It has been shown that the accumulation on tents of decaying leaves has brought about the rotting of fabric treated with chromium–iron. For many years a chromium–iron treatment has been applied to tentage duck used by the Canadian Army, although the degree of rot resistance shown by the treated duck has been of a low order and there has been considerable deterioration of tentage pitched in open country in Canada, through microbiological attack during the summer months (see Fig. 1). It should be pointed out that the chromium oxide contents of the fabrics concerned were exceedingly low.

The problem of a colourless rotproofing treatment having the efficacy of the treatments discussed above still remains to be solved. None of the colourless compounds examined in the present investigation showed satisfactory resistance to weathering, even when present in conjunction with wax. Other colourless compounds that have been investigated as rotproofers include salicylanilide, phenolic compounds, and organo-mercurials. These compounds have not been found to possess high efficacy under conditions favouring severe microbiological attack, and most of them show unsatisfactory weathering characteristics. However, some of these compounds, notably salicylanilide, have been successfully used as preservatives for cotton textiles during storage.

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PLATE I

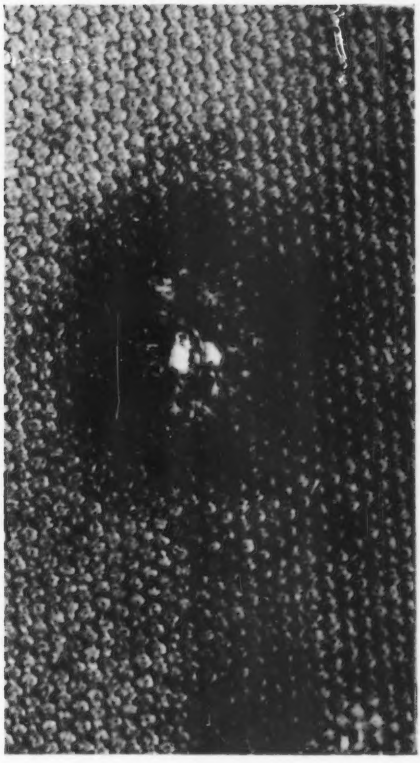

FIG. 1. *Army tent duck (12 oz.) taken from Canadian Army Tent, Circular, showing deterioration caused by microbiological attack occurring during use in Canada.*

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